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GRANITIZATION, MIGMATIZATION, AND FUSION IN THE NORTHERN ENTIAT MOUNTAINS. By Dwight F. Crowder

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BULLETIN OF THE GEOLOGICAL SOCIETY OF AMERICA
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Review Articles In Geology

A Plan for the Regular Publication of Invited Papers

By Committee on Review Articles in Geology

Critical review of published progress in a field or subject with the sole objective of arriving at a balanced evaluation and synthesis of current knowledge and understanding is a high and rewarding form of research endeavor. Indeed the writing and publication of such reviews is an essential part of the healthy growth of any scholarly discipline, for they provide the substratum of consolidated knowledge from which new inquiries can be more effectively made and integrated.

A well-balanced intellectual diet, then, should include both ample portions of original inquiry and factual data and an adequate seasoning of theoretical and synthetic works to stimulate and aid digestion. It is a proper concern, moreover, of a scientific community to assure such balanced fare by stimulating the better provisioning of items in short supply. Toward this end the Committee on Review Articles was founded in the National Research Council and perpetuated under The Geological Society of America.

Specifications for a good review article were outlined, and selected examples were given by the original Committee in its historical statement prefatory to the first three invited articles that appeared under this program (Bull. Geol. Soc. America, March 1953; Poldevaart, 1953; Bucher, 1953; Ingerson, 1953). Only three more articles (Sharp, 1954; Black, 1954; Pecora, 1956) have since been published under the auspices of that Committee, but its total influence is to be estimated in terms of numerous unidentified review articles by other authors in the pages of this Bulletin and elsewhere.

The present, and undersigned, Committee endorses the appraisal and challenge of its predecessors (Cloos and others, 1953). We conceive the ideal review article to be a critical, comprehensive, and balanced distillation of a problem or a field of interest—large or small. It is not so exhaustive as to load the bibliography with trivial references, or so impersonal as merely to summarize. Rather it aims at analysis and condensation of the significant published record and seeks to find in existing data the basis for new outlooks and future pathways of research. In order to assure the stimulating and cohesive effects desired, therefore, and in hopes of exemplifying high standards in scientific writing, we are making a special effort to select and schedule authors and subjects from the front ranks of competence and interest.

The articles that follow are only in part the fruit of our efforts, and not a very large crop to begin with, but we like them and we hope you will too. It is our present plan, approved by the Council, that the June number of the Bulletin will henceforth be a Review Articles Number, and that, when and if the volume warrants it, there will be a winter Review Number as well—perhaps eventually even a review journal, with provision for discussion and critical evaluations of recent major publications. All articles published under our auspices will be invited articles and will undergo review for suitability and technical content by members of the Committee and *ad hoc* critics before approval for identification as a Committee-sponsored paper.

Our aim is to underscore the objective and stimulate more of this type of research by assuring the regular appearance of papers which are identified as approximating our concept of a good review article. We do not suppose that all good review articles will appear in the Review Articles Numbers, or even that every article that does appear there will conform to our ideal. Rather, we intend that Committee-sponsored review articles shall all meet a high standard and that a large proportion of them will be truly superior. A collateral objective is the stimulation of critical reviews and syntheses of basic progress in geology, wherever published.

We solicit your co-operation in bringing to our attention prospective authors and subjects of leading quality and interest, and your evaluations of the results.

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BULLETIN OF THE GEOLOGICAL SOCIETY OF AMERICA
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GRANITE EMPLACEMENT WITH SPECIAL REFERENCE TO NORTH AMERICA

BY A. F. BUDDINGTON

ABSTRACT

Publications of the last 25 years that discuss the emplacement of granite plutons are reviewed, with special reference to North America. The plutons are classified according to emplacement in the epizone, mesozone, or catazone of the earth's crust. It is found that those emplaced in the epizone are almost wholly discordant; those in the mesozone complex, in part discordant and in part concordant; and those of the catazone predominantly concordant. Granite formed by granitization is considered to be minor or local in plutons of the epizone, common but subordinate in those of the mesozone, and a major factor in plutons of the catazone. The authors of the papers reviewed in general, however, infer that magma was either directly or indirectly the major factor in all the zones. Contrary to some current theories, this review emphasizes the great number and great total volume of granitic plutons emplaced as fluid magma in the epizone and their community of origin with lavas of similar composition directly associated in time and space. Magma is thus inferred to play the major role in Tertiary stocks and batholiths. There appears to be no discontinuity between plutons of the epizone and those of the mesozone, and a major role for magma is indicated for the latter also. The evidence is not clear as to whether plutons of the mesozone are continuous with those of the catazone, have roots in the catazone, or are pinched off from it. Batholiths emplaced in the mesozone are dominant in most basement complexes of Precambrian to Early Cretaceous ages.

SOMMAIRE

Les publications des 25 dernières années qui traitent de l'emplacement de plutons de granit sont passées en revue, en se référant spécialement á l'Amérique du Nord. Les plutons sont classés en fonction de leur emplacement dans l'epizone, la mesozone, ou la catazone de la croûte terrestre. On a découvert que ceux placés dans l'epizone sont presque complètement discordants; ceux dans la mesozone complex, en partie discordants et en partie concordants, et ceux situés dans la catazone concordants de façon prédominante. Le granit forme par le granitisation est considéré comme peu important ou épars dans les plutons de l'epizone, courant mais secondaire dans ceux de la mesozone, et d'importance majeure dans les plutons de la catazone. La plupart des auteurs de ces publications passées en revue déduisent cependant que le magma était, directement ou indirectement, le facteur le plus important dans toutes les zones. Contrairement é certaines théories courantes, cette étude met en évidence le grand nombre et le grand volume total de plutons granitique emplace sous forme de magma fluide dans l'epizone; aussi leur origine communal à celle des laves de composition similaire associées directement à elles dans le temps et dans l'espace. On en déduit donc que le magma joue le rôle de premier plan dans les batholithes et les stocks Tertiairies. Il ne parait pas y avoir de discontinuité entre les plutons de l'epizone et ceux de la mesozone, et, par consequent, on indique que le magma joue également un rôle important dans le mesozone. Il n'est pas clairement évident que les plutons de la mesozone forment une suit ininterrompue avec ceux de la catazone, qu'ils aient des racines dans la catazone, ou bien qu'ils se disjoindre. Les batholithes situés dans la mesozone dominent dans la plupart des complexes profonds de l'epoque Précambrienne jusqu' à l'epoque Crétacee inférieure.

ZUSAMMENFASSUNG

Es werden Veröffentlichungen der letzten 25 Jahre besprochen, welche die Position von Granit-Plutonen, besonders solcher von Nord-Amerika, behandeln. Die Plutone werden entsprechend ihrer Lagerung in der Epizone, Mesozone oder Katazone der Erdkruste Klassifiziert. Es zeigt sich, daß die Lagerung in der Epizone nahezu völlig diskordant ist, diejenige in der Mesozone dagegen komplex, teilweise diskordant, teilweise

konkordant, und diejenige in der Katazone vorwiegend konkordant. Granite, welche durch Granitisation geformt wurden, müssen in den Plutonen der Epizone als verhältnismaßig, selten oder nur örtlich angesehen werden, als regelmäßig, jedoch untergeordnet, in denen der Mesozone, und als ein Hauptfaktor in den Plutonen der Katazone. Die Autoren der besprochenen Veröffentlichungen kommen jedoch im allgemeinen zu der Überzeugung, daß das Magma, direkt oder indirekt, in allen zonen der Hauptfaktor war. Im Gegensatz zu einigen anderen umlaufenden Theorien betont diese Zusammenschau die große Anzahl und den großen Gesamtraum von Granitplutonen, welche als flussiges Magma in die Epizone eingedrungen sind und unterstreicht ihren gemeinschaftlichen Ursprung mit Lavamassen ähnlicher Zusammensetzung, mit denen sie zeitlich und räumlich in direkter Verbindung stehen. Das Magma spielt infolgedessen eine Hauptrolle in tertiären Granitstöcken und Batholithen. Es scheint keine Unterbrechung zwischen den Plutonen der Epizone und denen der Mesozone zu bestehen, und für die letztere scheint das Magma ebenfalls eine wesentliche Rolle gespielt zu haben. Die Beweise sind nicht klar, ob die Plutone der Mesozone in diejenigen der Katazone übergehen, ob sie Wurzeln in der Katazone haben oder ob sie von ihr abgeschnitten sind. Die in die Mesozone eingelagerten Batholite sind in den meisten Grundmassiven vom Präkambrium bis zur Unteren Kreide vorherrschend.

ЗАЛЕЖИ ГРАНИТА В СЕВЕРНОЙ АМЕРИКЕ

А. Ф. Буддингтон

Абстракт

Печатные труды последних лет, описывающие положение гранитных плутонов, особенно труды изданные в Северной Америке являются предметом настоящего обзора. Плутоны классифицированы согласно их положению в эпизоне, месозоне или катазоне земной коры. Было найдено что плутоны находящиеся в эпизоне почти полностью несовместимы; теже в месозонном соединении частью несовместимы и частью совместимы тогда как те в катазоне главным образом совместимы. Гранит образованный путем гранитизации разематривается как второстепенный или местный фактор в плутонах эпизона, обычный но второстепенный в плутонах месозона, и как главный фактор в плутонах катазона. В общем авторы статей настоящего обзора однако допускают что магма непосредственно или посредственно является главным фактором во всех зонах. В противоположность некоторым современным теориям рассмотренным в настоящем обзоре подчеркивается большое количество и большой объем гранитных плутонов внедренных в виде жидкой магмы в эпизоне и их средство по происхождению с лавами подобного же состава непосредственно связанными по времени и пространству. Повидимому не существует непрерывной связи между плутонами эпизона и плутонами месозона, при чем главная роль для магмы указана также для последнего. Еще не ясно являются ли плутоны месозона непрерывно связанными с плутонами катазона, исходят ли они из катазона или отщеплены от него. Батолиты, внедренные в месозоне играют главную роль в большинстве основных масс Прекамбриоповой вплоть до ранней Кретасовой эпох.

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Introduction and Acknowledgments

A wealth of detailed descriptions of the internal structure and external relationships of granitic plutons to country rock has been published since the reports (1931–1935) of Professor Grout's "Committee on Batholith Problems", the review by Daly (1933), and the memoir of Balk (1937). Read has meanwhile (1949; 1951; 1955; 1957) developed a philosophy of the origin and genetic relationships of granitic bodies under the phrase "The Granite Series" which is a major contribution. Read emphasizes that the mechanics of emplacement of granitic masses must be interpreted in the light of their regional setting. The writer proposes to amplify this idea further, largely in the sense of an essay review documented with specific examples, based preponderantly on the pertinent literature of the past 25 years that describes the granitic plutons of North America. The plutons of North America are emphasized because the author is better able to evaluate the implications of the literature on them; and because the phenomena of the plutons of North America and their interpretations have led to an emphasis on certain mechanics and conditions of emplacement that is different from that of much of the current European literature and deserves review and consideration. A few examples of plutons from outside North America will be cited to exemplify or accentuate certain ideas or phenomena.

The writer is indebted to Preston E. Cloud, Jr., H. H. Hess, F. F. Osborne, and Arie Poldervaart for friendly criticism and constructive suggestions. They should not, however, be held responsible for shortcomings of the review.

The problem of the origins of granite is necessarily a factor in the consideration of the mechanics of emplacement of plutons. Many geologists who believe that most granites are formed by "granitization" or "transformation" repeatedly emphasize that the problem must be solved by geology and field evidence. There is also the implicit inference that field geologists, with independent minds and familiar with the current ideas of granitization, will find granitization the best hypothesis to explain most or nearly all granites. Yet the North American literature of the past 25 years emphasizes strongly the role of magma either directly or indirectly in the problem of emplacement of plutons. This despite the fact that the authors quoted, more than 100, are field geologists who accept as valid concepts

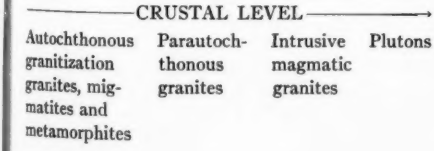
the potentiality of formation of granite by granitization as well as emplacement by plastic crystalline flow. A review of the literature, in general, makes it obvious that we do not yet have dependable criteria that are acceptable to geologists as a whole to distinguish between the products of the different mechanisms of emplacement. There would also probably be little dissent from the view that such geologic problems will *not* be solved by field geology alone, but by retention of what seems good in old ideas with constant rethinking and co-ordination of new hypotheses, of data from new experiments and new laboratory studies, and of new results of field geology aided by the rare new "flash of insight" idea.

In the discussion to follow the dividing line between a stock and a batholith will be taken as roughly 40 square miles as suggested by Daly. Granite, except where indicated otherwise by the context, will include the family of granitoids such as quartz diorite or tonalite and trondhjemite, granodiorite, quartz monzonite or adamellite, and granite or leucogranite and alaskite. The term pluton will be used here in a very general sense for any body of intrusive igneous (or "pseudo-igneous" by metasomatism or recrystallization) rock of any size or shape. Dikes, sills, and laccoliths will receive but passing mention. The term plastic crystalline flow here means flow of material which remains wholly or predominantly crystalline during thoroughgoing deformation and includes the concept of recrystallization through partial melting or solution and redeposition.

Read's "Granite Series"

Read's concept of the "Granite Series' may best be presented by excerpts from his writings.

(1957, p. 79) "Intrusions have been classed as pre-tectonic, syntectonic or post-tectonic. I have endeavored to codify these relationships in what I call the Granite Series (Read, 1949), a series which relates the nature and form of different types of granitic bodies with their place in the fold-belt and the time of their final solidification. The *Granite Series* can be represented thus:



Deep in the fold-belt are formed, at an early stage of orogeny, great complexes of granitization granites associated with migmatites and widespread regional metamorphic rocks. As the orogeny continues, a part of these autochthonous granites becomes partly unstuck from its surroundings and moves higher in the fold structure. This process continues with the movement of true intrusive and magmatic portions late and high, and culminates in the emplacement of the granite plutons, highest and latest, pushing their way as almost solid bodies even into the post-orogenic sediments." (1951, p. 21) "The resulting parautochthonous granites show variable marginal relations, in some places migmatitic, in others characterized by an aureole of thermal type. This movement out of the migmatitic-metamorphic setting may continue till the genetic ties are completely severed and *true intrusive granites* emplace themselves in higher levels of the crust maybe as magma but more likely as migma. The final term of the granite series is represented by the high-level *plutons*, intrusive into non-plutonic regions late in the history of the orogen concerned. . . . The plutons are the domain of the Granite-tektonik of the Cloos school and, as their emplacement produced considerable folding and distortion in the country rock surrounding them, they came in as almost dead bodies."

The writer believes that Read's discussion needs some major revision. Plutons with "granite-tektonik" are not the final terms of the granite series. On the contrary they belong almost wholly to the mesozone where, as multiple units, they may form huge batholithic complexes. The final terms of the granite series are the plutons of the epizone. Read minimizes as "few", "puny", and "nearly dead" the bodies emplaced in the upper levels of the crust. This is wholly inconsistent with the number, size, significance, and the evidence for mobility and fluidity of most plutons emplaced in the epizone of the crust in North America. Knopf (1955, p. 697) estimates that plutons of Tertiary age in North America and Greenland (all emplaced in the epizone) have a total area of 52,000 square miles.

Hans Cloos (1931) has presented a succinct pertinent discussion of the possible structural relationships of plutons at different depths. A summary prepared by S. W. Sundeen (1935, p. 48–49) is quoted here

"In a single mass the inner tectonics differ at different horizons. In the upper horizon there are poor, elusive structures in irregular branching stocks. In the moderate depths there are well-formed arches, schlieren domes, partitions or pendants of wall rock and cleavage with border deformation and mylonites; with or without a stretching of the border spalls. In the deep zone there are arches of gneiss. The whole region is deformed and moves with the magma as an ill-defined unit; the rocks are largely recrystallized, and intrusion

occurs not only before and during crystallization but in part after. There is thus a lack of any small dynamic border zone and a lack of fracture surfaces, border spalls and most other features of the moderate zone. Cloos sketches a vertical section of a composite of these three horizons, each mass smaller and drained up from the one below, and with less foliation than the one below; but does not deny that a single mass may grade downward without much change in horizontal section into the conditions of the deeper zone."

Zones of Emplacement

The granite emplacement series will be discussed with emphasis on the internal and external structure of the plutons within different temperature–depth or intensity zones of the crust. Under the simplest hypothesis the intensity of regional metamorphism may be expected to increase somewhat uniformly with depth and therefore afford an indicator of the depth. The site and period of granite emplacement, however, is not one of static conditions but of dynamic changes in the environment. This is especially true for the mesozone. The intensity of regional metamorphism in belts away from the intrusives may still be used, however, as a suggestive clue to the depth zone. (*See also* Michot, 1957). Inasmuch as we are particularly interested in the physical conditions of the country rocks at the time and in the region of emplacement, the upper and lower limits of each zone will have a considerable range of depth for different regions and at different times in development. The depths for plutons with similar characters will depend on the temperature, pressure, relative mobilities of the country rocks, and other factors. The term zones as used here thus refers actually in substantial part to *intensity zones* rather than strictly depth zones. At the same level in the mesozone a batholith may be emplaced discordantly in only warm country rock during early stages and conformably in hot rock during late stages, especially in the roof. A predominantly mesozonal pluton may have characters peculiar to the catazone in the roof portion. In some examples the estimation of the physical conditions may be difficult and little better than a guess. Nevertheless examples for which at least fair to good data are available afford the basis for a reasonably consistent picture and afford some additional insight into the problems of emplacement.

Michot (1956, p. 28) suggests that the epizone may be taken as extending from the surface to a depth of 10 km. The mesozone and catazone will be successively below this.

The development of the greenschist facies of metamorphism in rocks could be considered as a characteristic phenomenon of the mesozone. Fyfe, Turner, and Verhoogen (1958, p. 218) estimate that it is unlikely to develop below a temperature of about 300°C. and above a depth of about 10 km. Their curves (p. 182) for rise of temperature with depth suggest that at a depth of about 10 km in a great thickness of sediments, after depression in the earth's crust, the temperature might rise to about 250°C., and where the temperature had been increased by magmatic intrusion it might be as high as 450°C. A rise of temperature in the country rock above an intruding magma is strongly implied by such data as that given by James (1955). The magma may thus be emplaced in rock of temperature higher that that otherwise appropriate for the general region. A depth commonly of 4 miles but with occasional extension, perhaps, to 6 miles seems a reasonable estimate for the base of the epizone.

The depth of the base of the mesozone or top of the catazone where the amphibolite facies starts must likewise have a substantial range, perhaps from as shallow as 5 miles to as deep as 10 miles. Wegmann (1935) estimated the minimum depth of the "migmatite front" at 10 km. The temperature range for the mesozone may be estimated to vary from about 250°–350° at the top to 500°C. at the base.

Tuttle and Bowen (Adams, 1952, p. 38) wrote that "It is improbable that many granites reaching the light of day have crystallized at depth greater than 9 miles". This seems slightly low. The possibility that erosion has exposed levels at a maximum a few miles deeper than this must be considered, but in general it is probably of the right order of magnitude. Gutenberg (1957) cites figures of 35 km for the depth of the "granitic" crust beneath the Alps and 25–30 km beneath the Sierra Nevada. If this is assumed to indicate the depth of the down folded sial, and if reasonable estimates are made for the thickness of eroded material a figure of about 25 miles is arrived at as the normal maximum depth for sialic material. Assuming further that the minimum thickness of sialic basement complexes in the continental shields is about 10–12 miles, the inference may be drawn that present levels of erosion have rarely exposed rocks that were ever at a depth greater than about 12–15 miles.

The rocks of the granulite facies in the Grenville belt appear to represent those formed at some of the deepest depths now exposed in North America. They are estimated to have formed between 600° and 700°C. Fyfe, Turner, and Verhoogen (1958, p. 182) give a curve that indicates that a temperature range of 600°–700°C. could be reached at depths of 9–13 miles where the gradient had been increased by magmatic intrusion. Rosenquist (1952, p. 102) estimates the minimum depth for the development of the granulite facies in this temperature range as 9–10 miles.

The predominance of mesozonal batholiths in basement complexes, however, indicates that only locally has erosion cut very deep.

Possible depth relationships for the zones are shown in Figure 1.

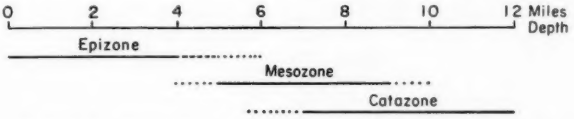


FIGURE 1.—SCHEMATIC RELATIONSHIPS OF EMPLACEMENT ZONES

There is in the western Cordillera of North America a rough correlation between the structural relationships and zones of emplacement of the plutons and their ages, especially for those of Late Jurassic and younger age. Plutons of Tertiary age as now exposed were exclusively emplaced in the epizone and may be associated in space and general time with volcanic rocks of equivalent composition and often emplaced in them; those of the Late Cretaceous are also emplaced in the epizone, but there are *more* large plutons; the great composite early Late Cretaceous (?) Southern California batholith has characters transitional between those of the epizone and those of the mesozone, whereas the composite stocks and batholiths of the Late Jurassic and Early Cretaceous were emplaced in the mesozone with earlier members of the largest batholiths emplaced in the catazone.

Similarly, in the Appalachian orogen, the post-Pennsylvanian plutons were all emplaced in the epizone, whereas many earlier plutons of Devonian age were intruded in the mesozone, transitional mesozone-catazone, or locally perhaps the catazone.

For rocks older than the Tertiary, however, there is no necessary systematic relationship between age of rocks and the depth at which they were emplaced. Unmetamorphosed plutons 2.5 billion years old may be of the type emplaced in the mesozone, as in the Keewatin belt of the Canadian Shield where erosion to only moderate depths is indicated.

PLUTONS OF EPIZONE

"Dr. Hutton's theory of granite . . . at the same time that it conceives this stone to have been in fusion, supposes it to have been, in that state injected among the strata already consolidated." John Playfair, 1802.

Introduction

It is rare that estimates are given in the literature of the depths at which the present exposed parts of a pluton were intruded. Tertiary intrusions as now exposed may be expected to have been emplaced within the epizone; the time for subsequent erosion has been too short to permit deep erosion. A review of the literature shows that Tertiary intrusions have the following characters, and these will be used as criteria in classifying intrusives in the epizone of older ages.

Tertiary stocks and batholiths are largely or wholly discordant to the country rock no matter whether they occur in Precambrian schists and gneisses or in folded Paleozoic and Mesozoic sediments, or, as is common, in gently dipping Tertiary volcanic rocks. Occasionally, as in the Gold Hill stock in Nevada (Nolan, 1935, p. 43–48), part of the walls are controlled by preintrusive faults. They may occur in limestones, a type of rock peculiarly resistant to granitization, without any suggestion of relics or inheritance by replacement. A few granitic plutons may be effectively homogeneous in composition, but most are of composite character caused by a successive series of magma emplacements of diverse composition. The diversity is commonly from syenite or monzonite to granite, or from diorite through quartz diorite, granodiorite, and quartz monzonite to granite. Quartz diorite commonly does not form as large a part of plutons in the epizone as it does in those of the mesozone. Locally or in a few plutons the diversity may

be due in part to incorporation, more or less in place, of country rock, especially in border or roof zones, but this is usually relatively unimportant. Roof pendants are common. Many of the plutons are effectively homophanous without lineation or foliation. Some have a primary linear structure, but well-developed planar foliation is uncommon and, where it occurs, is usually restricted to local border facies or is indistinct.

The orientation of lineation in the Jamestown, Colorado, granodiorite stock has been studied by Goddard (1935). He finds that the stock is elongated N.–S., that the lineation along the western part plunges about 70°–80° and in a re-entrant protrusion on the east has a gentler plunge of about 35°–60°. Grout (quoted in Calkins and Butler, 1943, p. 35–36) studied the lineation of the Alta stock in Utah and shows the linear structure plunging in general 80° or steeper in the border zone and gently in the core. The lineation of both stocks thus suggests steep upward flow in the border zones. Grout and Balk (1934, p. 885) find that lineation in much of the Boulder batholith is elusive, but most has a pitch of about 70°, and a steep conformable upward rise is suggested. Both the Alta and Jamestown stocks and also the Mount Princeton batholith (Dings and Robinson, 1957, p. 30) have associated dikes with gently plunging lineation suggesting subhorizontal flow. Other types of orientation of flow lines such as arches of flow lines and disconformable flow lines at an angle to the walls have been referred to by Balk (1937, p. 50–54, 60–63, 69–78). The arches of flow lines may in some examples, at least, be suggestive of an arched roof.

Moehlman (1948, p. 118) and others have referred to Tertiary plutons whose walls converge downward.

Volcanic rocks are commonly associated in close genetic relationship with Tertiary plutons, but they need not be with plutons of the deeper part of the epizone. Characteristically, at least, part of the volcanic rocks will have compositions comparable to that of the facies of the plutons themselves although the quantitative ratios may be different. Alper and Poldervaart (1957) have studied the Animas stock in New Mexico and the volcanic rocks it intrudes and have shown that not only is the chemical and mineral composition similar but the zircons of both the tuff and the pluton have similar habits.

The country rock, outside of the contact-metamorphic zones, may be relatively unmetamorphosed. If folded and regionally metamorphosed there may be independent evidence that the country rocks were only moderately warm and at shallow depths at the time of emplacement. Zoning of associated mineral veins on a regional scale is common, as are veins of epithermal or xenothermal character in the upper part of the epizone. Zoning of veins by repetitive introduction of solutions of diverse compositions during repeated structural reopenings is common. Peripheral outward deformation of the side walls is a feature of some epizonal plutons. It ranges from locally strongly deformed peripheral folds to gentle parallel peripheral folds; outward thrusting is inferred in one example; rarely there is a local thin zone of foliation or local thin layer of slight plastic crystalline flowage in contact-metamorphic zones or local minor drag folding. Most of the plutons are small, but there are also nevertheless many batholiths. The Paleozoic White Mountain batholith in New Hampshire associated with cauldron-subsidence origin has an outcrop area of 680 square miles, the Upper Cretaceous Boulder batholith an area of 1200 square miles, and the Tertiary Cordillera Blanca batholith of Peru is more than 75 miles long (Egeler and De Booy, 1954). The emplacement of stocks and batholiths associated with ring-dike complexes and cauldron subsidence is uniformly attributed by all authors to subsidence, either subcolumnar block sinking or block or piecemeal stoping.

Reference for comparative purposes may be made to the Cenozoic Slaufrudal stock 2 by 7½ kilometers in diameter, that cuts basaltic lavas with intercalated rhyolitic volcanic rocks in Iceland. Cargill, Hawkes, and Ledeboer (1928) describe the stock as consisting of miarolitic granophyre, in part with granitic texture. They suggest that the stock was emplaced by sinking of the replaced mass "en bloc" and that a distinct semihorizontal layering of the intrusion indicates intermittent subsidence, the stock growing by the addition of successive sills or caps. Relations are exceptionally well shown in steep topography.

Many other stocks and batholiths have a domical or a broad arch-shaped roof. This is commonly due in part to angular steplike transection of the roof to yield this kind of shape, in part to doming of the roof either by simple doming, or by doming accompanied by faulting in the roof due to distention.

The earlier members of a complex pluton, in small or moderate volume, will show chill zones against country rock. Dikes, apophyses, or small satellitic stocks related to large volumes of rock will commonly show chill zones or porphyritic characteristics. Many large masses or later members of a composite stock or batholith show no chill zones. There is often a set of late-stage aphanitic or porphyritic dikes. Associated lamprophyre dikes are also common. Distinct pegmatite veins are typically rare or minor although small pegmatitic nests may occur locally. Aplitic veinlets may be present, but aplite dikes or facies are not commonly abundant in the stocks. In some of the batholiths, however, aplite or equivalent alaskite may be well developed, as in the Boulder, Seagull, and Ackley (White, 1940) batholiths. Miarolitic structure is common, especially in leucogranite or alaskite, and it may have pegmatitic facies associated locally. Many aplite dikes are restricted to the border zone of the pluton where they occur both in the roof and in the adjacent igneous rock. Relatively flat-lying sheets of alaskite occur in the Seagull batholith, Yukon Territory, and of micropegmatite in the batholith of the Casto quadrangle, Idaho.

Granophyre may also occur locally as sheets, stocks, domical roof facies of stocks, or as metasomatized country rock. Granophyre, in general, occurs exclusively in the epizone.

Occasionally stocks of the epizone may be accompanied by satellitic laccoliths (Hunt, 1956; Strobell, 1956).

Emplacement predominantly by metasomatism is uncommon in the epizone and will be discussed under the title Pseudo-igneous Emplacement. Several plutons, however, do have an extensive aureole of granite or granite gneiss resulting from granitization of sandstone or metaquartzite. Contacts of pluton and country rock are normally sharp.

Oftedahl (1953, p. 71–74, 92–93) has interpreted the central nordmarkite and monzonite facies of the central part of the Sande stock in southern Norway as the product of assimilation of lavas by an ekerite magma more or less in place.

Such criteria as lack of contact metamorphism and contact metasomatism, lack of chill zones, and the presence of evidence for upward drag of wall rocks have been inferred (Read, 1951, p. 9–10; Tweto, 1951; Hunt, 1953, p. 165· Drewes, 1958, p. 233; Mackenzie, 1958, p. 69) to indicate that many plutons of the epizone have been emplaced as highly viscous magma at relatively low temperatures (600°C. or lower). This interpretation is satisfactory for many porphyritic intrusives with an aphanitic matrix, but we need more data to be sure it is appropriate for plutons of almost exclusively phaneritic rock. Most plutons of the epizone do have accompanying evidence of contact metamorphism and contact metasomatism. Andalusite is developed in shales and wollastonite locally in limestone at many contacts. Pyroxene intermediate between hedenbergite and johannsenite is not uncommon (Allen and Fahey, 1957). Tourmaline is common in many aureoles of epizonal stocks. Many epizonal stocks have at least local miarolitic facies, and they may be phaneritic throughout. These facts are consistent with the probability that the liquid phase of the magma of such plutons was relatively fluid because of its content of volatiles during part or all of its period of crystallization. An excellent comparison of the characteristics of highly viscous and less viscous magma emplacement in sills has been given by Tweto (1951).

In a few examples the smaller plutons are accompanied by a small amount of breccia whose origin is in part interpreted as an explosion breccia and in part as due to upward drag of magma. Examples are a breccia of slightly rounded fragments of sedimentary rocks and of porphyry, in a matrix of similar comminuted rock associated with a diorite stock in the La Plata district (Eckel, 1949, p. 39) and breccia zones on one side of a granodiorite stock (Goddard, p. 383–384). Tweto (1951, p. 526–528) has described an intrusion breccia as an advance guard of porphyry sills, formed by explosive intricutsion of fluids or tenuous magma. The breccia may consist of fragments of country rock and of chilled porphyry in a shale matrix or of dirty contaminated igenous material.

The magmatic origin of many salic dikes, stocks, and laccoliths emplaced in the epizone is indicated by the inclusions of deep-seated Precambrian rocks which they contain where emplaced in overlying beds. Examples are the quartz diorite porphyry laccolith described by Rouse (1933, p. 145–146) emplaced in Tertiary volcanic rocks with inclusions of Precambrian rocks which have been brought up for a minimum of 2½ miles, the inclusions of Precambrian rocks in monzonite-diorite porphyry stocks, sills, and sheets emplaced in

Mesozoic beds described by Eckel (1949, p. 34, 41), an example cited by Powers (1915, p. 166–168) in Vermont where bostonite dikes in Middle Ordovician shales contain inclusions of underlying Precambrian rocks, and similarly that by Buddington and Whitcomb (1941, p. 78–79) from New York where small laccolites and sills of quartz bostonite and rhyolite porphyry emplaced in Ordovician shales contain fragments of underlying Cambrian sandstone together with rare fragments of Precambrian basement material.

Some of the Tertiary laccoliths are so closely associated with volcanic rocks that they can confidently be considered to belong to a volcanic association. Hunt (1956, p. 43) writes concerning the laccolithic mountains of the Colorado plateau that "it seems likely that most of the larger stocks in the laccolithic mountains reached the surface and erupted, although probably none of them extruded any great quantity of lava or pyroclastic materials". A paper by Rouse *et al.* (1937) also portrays probable relationships between laccoliths and volcanic rocks. The major bodies originally described by Gilbert as laccoliths are now interpreted by Hunt (1956, p. 42–45) as the upper part of stocks, the latter up to about 2 miles in diameter. The Three Peaks laccolith, Utah, about 5 miles in diameter, has been studied in detail by Mackin (1947). He finds that the Upper Cretaceous (?) laccolith was emplaced under a cover that ranged from 2000 feet to a possible maximum of 8000 feet. The laccolith consists of quartz monzonite porphyry, generally holocrystalline but with some glass in the groundmass near contacts. He infers that the chilled borders and the glass prove that the mass was emplaced as magma. Some of the quartz monzonite porphyry is finely miarolitic.

The numerous diorite and monzonite porphyry sills of the La Plata district (Eckel *et al.*, 1949, p. 34) also belong among the volcanic bodies.

Granitic Stocks and Batholiths Associated with Ring Dikes and Cauldron Subsidence

Introduction.—Granitic stocks and batholiths associated in time and space with ring dikes and cauldron subsidences in direct relation to volcanic rocks occur in many different belts of different and widely spread localities in the world. They are very pertinent to our problem. At many of these localities there are also independent larger discordant plutons, associated with those directly due to cauldron subsidence, and inferred to be emplaced by block foundering or stoping. The prototype of this kind of complex is the Devonian Glen Coe cauldron subsidence and the associated Starav granite batholith described by Clough *et al.* (1909). Other examples of discordant batholithic intrusion following ring dike and stock emplacement are the Conway granite pluton of the White Mountain batholith complex (680 sq. miles, Fig. 2), the Drammen and other batholiths (Fig. 3), and the Jos-Bukuru pluton complex (285 sq. miles) of northern Nigeria (Jacobson *et al.*, 1958, p. 11, Pl. VII).

Billings (1943) writes that he found descriptions in the literature of 115 ring dikes and 30 ring-dike complexes. He states that 11 of the 30 ring-dike complexes have a central block of volcanic rocks that has subsided. These central volcanic rocks are flows and pyroclastic rocks ranging in composition from basalt through andesite and trachyte to rhyolite; they are, he believes, comagmatic with the rocks in associated ring dikes. He further states that 17 of the 30 ring-dike complexes possess what may be called a central stock, and the central stocks usually consist of quartz-bearing rocks, commonly quartz syenite or granite. Belts in Nigeria and Southwest Africa and examples elsewhere have been described since Billings wrote so that many more ring-dike complexes are now known.

Examples have been chosen from the literature to exemplify the foregoing principles. Before presenting these we might refer to some of the largest masses of acid volcanic rocks which are believed to be of magmatic origin.

The volcano-tectonic depression of the Rotorua-Taupo graben in New Zealand (Marshall, 1935) is about 60 by 15–20 miles in areal dimensions, with several thousand feet of depression and about 2000 cubic miles of welded tuff (ignimbrites) occupying a basin of approximately 10,000 square miles. This would be about equivalent to a batholith of 200 square miles and 10 miles depth. Again, Westervelt (1952, p. 565) has described a Middle Pleistocene rhyolitic tuff blanket in a fault trough in the Lake Toba area of North Sumatra covering 25,000 sq km and with a volume of 2000 cu. km. These are inferred to have formed as a result of the initial breakthrough of a comparatively shallow acid magma chamber underlying a pre-existing tectonic

depression. Ross (1955) has pointed out that pyroclastic rocks of rhyolitic, dacitic, quartz latitic, and some of latitic composition are present in many regions of the world, in volumes which dwarf many batholiths. Larsen and Cross (1956, p. 94) have estimated that the Miocene Potosi volcanic series of the San Juan volcanic rocks in Colorado contains 2300 cubic miles of rhyolitic volcanic rocks and 3000 cubic miles of quartz latite volcanics. The rhyolite volcanic rocks are the equivalent of a granite batholith 230 square miles in area and 10 miles deep. Stocks of monzonite and granodiorite emplaced in the same general period of time as the Potosi lavas are associated with them and range in size from necks up to plutons 2 by 5 miles in diameter.

Late Tertiary cauldron subsidence and intrusion.—The youngest cauldron-subsidence complexes may be expected to be among the least eroded and give the clearest evidence of belonging to a volcanic association.

Two such complexes from the United States will be described.

MEDICINE LAKE HIGHLANDS CALDERA, CALIFORNIA: Where erosion has not cut too deeply, cauldron subsidences occur at the surface as in the Pliocene(?)-Pleistocene(?) volcanic rocks of the Medicine Lake Highlands, California, described by Anderson (1941, p. 358–361). The caldera is an elliptical area about 4 by 6 miles in diameter in a shield volcano of platy olivine andesite about 20 miles in diameter. The rim of the caldera is outlined by nine volcanic vents from which platy andesite (±10 per cent normative quartz and ±61 per cent calcic oligoclase) has issued. The floor of the caldera is inferred to have sunk at least 500 feet through collapse of a central block coincident with ring-dike intrusion and the eruption of andesitic lavas squeezed up the marginal fractures. This hypothesis would necessitate a stock of magma below with the composition of a quartz diorite. Later lavas from the vents include olivine andesites, dacites, and rhyolites and are inferred to represent continued differentiation products discharged from later local vents in part spaced along the margin of the depressed block. This would imply in part the existence of magma below which could yield granitic masses on consolidation. The nature and tectonic relationships of these volcanic rocks may be considered as surface manifestations of ring-dike complexes and associated deeper stocks and batholiths.

SILVERTON CALDERA, COLORADO: Another significant volcanic unit is the Silverton caldera, described by Burbank (1941). The Silverton caldera is a minor unit areally and structurally of the volcanic field of the San Juan Mountains. The caldera was formed in the late Tertiary by gradual downwarping and faulting of a large shield-shaped block of crust about 8 miles in diameter. As downwarping of the basin became accentuated with thickening of the volcanic accumulations, ring faults and associated radial fractures developed. Intrusive bodies forced their way upward along certain more strongly accentuated regional rifts, and great numbers of smaller intrusive bodies and volcanic pipes penetrated the broken rocks of the fault ring. Burbank suggests that both the rock alternation and the concentration of intrusive bodies indicate that at moderate depths below the surface the margin of the caldera is underlain by a more or less continuous ring of intrusive rock. The intrusive rocks consist of gabbro-diorite, andesite, latite, quartz latite porphyry, and rhyolite. The volcanic rocks consist of andesite, "latites", quartz latite, and rhyolite. Larsen and Cross (1956, p. 227) describe one of the quartz monzonite stocks as 2 by 5 miles in diameter.

Early Tertiary cauldron subsidence and plutons.—Early Tertiary plutons associated with cauldron subsidence may be expected to include some which have been eroded to a deeper level than those of the Late Tertiary, and this is the fact.

QUITMAN COMPLEX: The following summary of the Early Tertiary Quitman complex is based on that by Huffington (1943). A series of lava flows ranges in composition from basalt to trachyte and rhyolite; rhyolites are most abundant. They are associated with pyroclastic rocks, and the whole has an approximate thickness of 3500 feet. Late basining, probably due to magmatic subsidence below the volcanic rocks, has dropped the central portion of the volcanic rocks approximately 4500 feet. A discontinuous elliptical ring of intrusives around the volcanic rocks is interpreted as a ring dike about 4 miles in diameter. The earliest intrusion in the area was a diorite; the ring-dike intrusion averages quartz monzonite. There is a related stock of quartz monzonite adjacent to the ring dike. The quartz monzonitic stock is subcircular with a diameter of about 3.5 miles and is separated from the parts of the ring dike by a septum about half a mile wide of Lower Cretaceous sedimentary rock. Belts of aplite and granite porphyry are localized along the contact of the quartz

monzonite. Granites form less than 10 per cent of the plutons, and monzonite and syenite each about 10 per cent. The ring dike is inferred to have been emplaced in large part by stoping along the ring fracture.

and one of late Karroo age in Southwest Africa (Korn and Martin, 1954). These plutons occur in the "epizone" of the crust and can approximately be considered to belong to a volcanic association. In addition to the annular

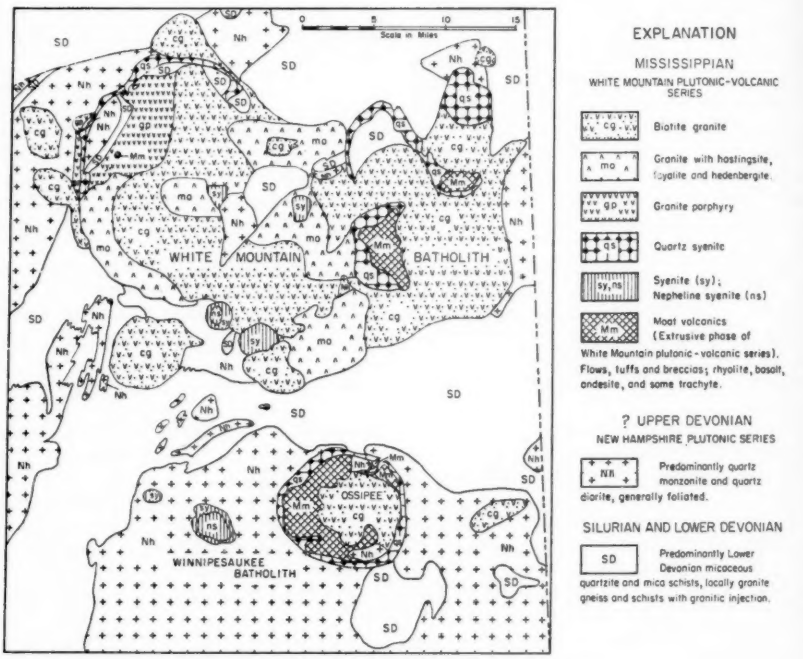

Scale in Miles
0 5 10 15
WHITE MOUNTAIN BATHOLITH
OSSIPEE
WINNIPESAUKEE BATHOLITH
EXPLANATION
MISSISSIPPIAN
WHITE MOUNTAIN PLUTONIC-VOLCANIC SERIES
Biotite granite
Granite with hastingsite, fayalite and hedenbergite.
Granite porphyry
Quartz syenite
Syenite (sy); Nepheline syenite (ns)
Moat volcanics (Extrusive phase of White Mountain plutonic-volcanic series). Flows, tuffs and breccias; rhyolite, basalt, andesite, and some trachyte.
? UPPER DEVONIAN
NEW HAMPSHIRE PLUTONIC SERIES
Predominantly quartz monzonite and quartz diorite, generally foliated.
SILURIAN AND LOWER DEVONIAN
Predominantly Lower Devonian micaceous quartzite and mica schists, locally granite gneiss and schists with granitic injection.

FIGURE 2.—NEW HAMPSHIRE BELT OF PLUTONS

Ossipee complex ring dike and biotite granite stock of cauldron subsidence; White Mountain batholith of cauldron subsidence and coalescing rim fracturing; both Mississippian (?) of epizone; and older Winnipesaukee batholith of transitional (?) mesozone-catazone; Modified after M. P. Billings, 1956, N. H. Planning and Development Commission, Division of Geol. Sci., Harvard University and U. S. Geological Survey

Permian, Mississippian(?), and Devonian plutons associated with cauldron subsidence.—Four great belts, three of them more than 200 miles long, each with numerous granitic stocks, batholiths, and ring-dike complexes in direct tectonic, geographic, and time relationships with volcanic rocks of related compositions, have been described in recent years. The belt of Tertiary ring dikes and caldera subsidences with associated granite stocks of Scotland should also be noted. The four belts include that of New Hampshire (Billings, 1945; 1956) of Mississippian(?) age, the Oslo district in Norway (Holtedahl, 1943; Oftedahl, 1953) of Permian age, a belt in Nigeria (Greenwood, 1951; Jacobson *et al.*, 1958), dikes they range in size from small plugs and dikes to batholiths underlying as much as 680 square miles. The rocks of these belts may be thought of as representing in part levels of deeper erosion than the Tertiary plutons and in part the rise of large masses of granitic magma to relatively high levels.

Chapman and Williams (1935, p. 507) find that granite forms more than 78 per cent of the plutonic complexes of the New Hampshire belt, syenite and quartz syenite 20 per cent, and gabbro, diorite, and monzonite less than 2 per cent. Jacobson *et al.* (1958, p. 7) estimate that granite forms 94 per cent of the plutons of the belt in Nigeria and mafic to intermediate rocks only 6 per cent. By way of comparison

granite and granophyre form 63 per cent of the area of intrusive rock in the belt of Tertiary plutonic complexes of the British Isles, gabbro and dolerite 33 per cent, and ultrabasic rocks 3 per cent according to Richey (1948, p. 55).

NEW HAMPSHIRE BELT OF MISSISSIPPIAN(?) PLUTONS: The ring-dike complex of the Ossipee Mountains, New Hampshire (Kingsley, 1931), has one of the most nearly perfect ring dikes of the New Hampshire belt and exemplifies the general character of the complexes (Fig. 2). The ring dike is described as subcircular with a diameter of a little more than 8 miles and is composed of porphyritic quartz nordmarkite (13 per cent normative quartz). Within the central complex is an arc-shaped mass of the Moat volcanic rocks. These have an approximate thickness of 7000 feet and consist of basalt (4 per cent normative quartz), andesite (13.4 per cent normative quartz), and quartz porphyry flows, and equivalent tuffs and breccias. The remainder of the central complex, except for a small block of country rocks, is composed of a coarse-gained biotite granite (25.8 per cent normative quartz). Kingsley estimates that the minimum subsidence of the volcanic rocks on the borders is 4500 feet and in the center 12,500 feet. The biotite granite is inferred to have been emplaced as a result of either piecemeal stoping or a columnar-block subsidence.

The White Mountain batholith (fig. 2), another member of the New Hampshire central complexes, is significant because of its size. The following description is condensed from that of Billings (1928). The batholith lies about 4 miles north of the Ossipee Mountains complex. It underlies about 680 square miles and consists predominantly of granite with subordinate nordmarkite and great blocks of volcanic rocks, from a few to 8 miles in diameter, that have settled into the batholith. The volcanic rocks consist of siliceous flow rocks and interbedded tuffs and breccias to a thickness of about 11,800 feet. The siliceous flows are largely comendites (24–33 per cent normative quartz) or quartz porphyries. Trachyte (18.3 per cent normative quartz) also occurs. The plutonic phases include a small mass of diorite, nordmarkite (4–13 per cent normative quartz), and granite (23.6–28.5 per cent normative quartz). Some nordmarkite porphyry occurs as small satellitic stocks or as chilled border facies whose groundmass is dense. It is noteworthy that the extrusive comendites are comparable to the plutonic granite and the extrusive trachyte to the plutonic more siliceous facies of the nordmarkite. The volcanic rocks seem to have settled at least 5000 feet and probably at least 17,000 feet in one area since they do not occur in the adjoining region. The emplacement of the batholith is inferred to result from roof subsidence. Magma moved upward along great fractures and issued at the surface as great flows and pyroclastic deposits.

The belt of epizonal plutons is slightly discordant to the trends of the older country rocks.

OSLO BELT OF PERMIAN PLUTONS: The Oslo, Norway, belt of cauldron subsidences or ring-dike and central complexes has been described by Holtedahl (1943) and Oftedahl (1952; 1953). It is of such general significance that the writer cannot refrain from including a summary here. (*See also* Figure 3.) The plutonic complexes were emplaced in a lava plateau consisting of 2000–3000 m of basaltic and rhomb porphyry flows. The plutonic phase began with the consolidation of larvikite plutons, the magma of which corresponds to that of the rhomb porphyries. During later periods, with the formation of syenitic and granitic stocks there occurred the cauldron subsidences. Quartz porphyry annular dikes occur in three of the four described cauldrons as an early phase of intrusion.

The Oslo belt is very instructive because of the association of large batholiths of larvikite, nordmarkite, and biotite granite which form a belt about 200 km long; the four major cauldron complexes lie within the central part of this belt (Oftendahl, 1953, Fig. 1). One of these batholiths, the Drammen biotite granite (Oftedahl, 1953, p. 103), encloses the Drammen cauldron in the form of a huge cylindrical block or roof pendant. The biotite granite magma is younger than the rocks of the cauldron, and the stoping followed the ring fault nearly exactly. It has a quartz porphyry border against the effusives of the Drammen cauldron. The Drammen pluton is about 55 km long. Against the rocks of the Giltrevann cauldron it has a border facies of quartz porphyry with an aplitic groundmass. Oftendahl (1953, p. 58) further suggests that the granite magma was at a relatively high temperature, perhaps superheated. An ekerite batholith is younger than the rocks of the Sande cauldron. The ekerite is full of pegmatite nests and has a porphyritic border zone. Holtedahl (1951, p. 90) concludes with respect to the mechanism of emplacement of the batholiths that "huge subterranean crustal blocks sank to an

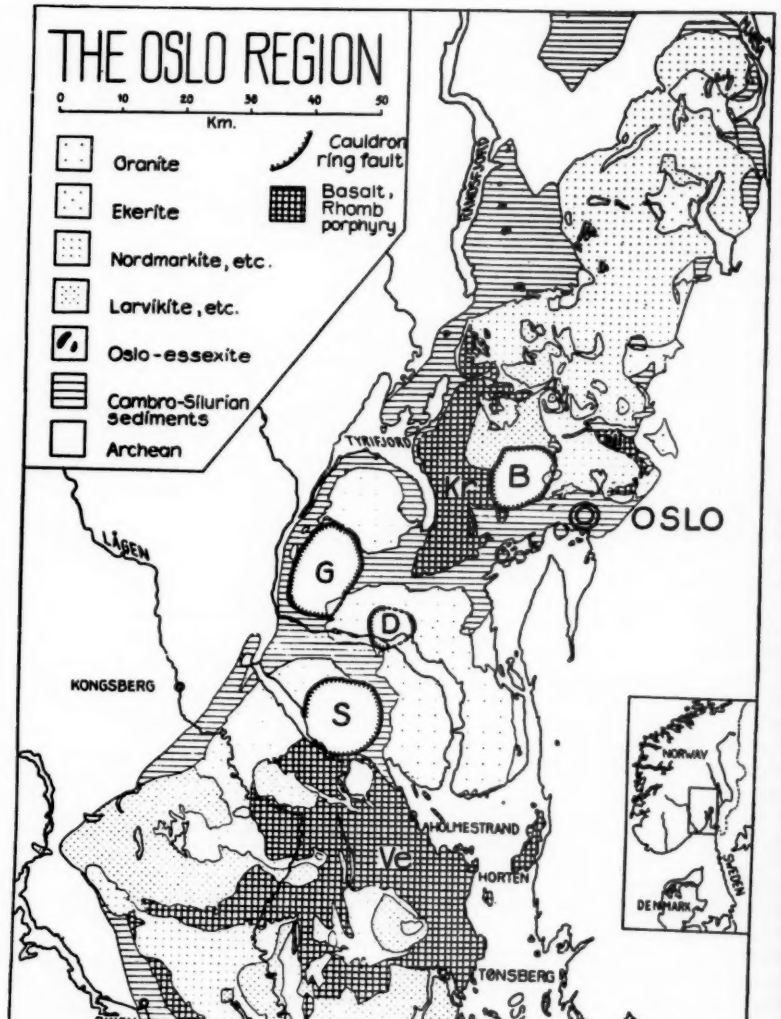


FIGURE 3.—OSLO REGION, NORWAY

Four Permian complexes (B, D, G, S) of lavas, ring dikes and stocks of cauldron subsidence, and associated younger discordant batholiths; all of epizone. After Oftedahl (1953)

unknown depth along curved fracture lines, with magma occupying the vacated space". Oftedahl (1952, p. 58) infers a monzonitic magma batholith at least 100 km long and 20–40 km wide, slightly superheated, to explain the rhomb porphyry lava flows. He further suggests (1952, p. 60) that stoping normally was arrested close to the surface (about 100–500 m below the surface), but occasionally the magma stoped its way clear to the surface to form areal eruptions.

Stocks Primarily by Cauldron Subsidence, but Accompanied by Outward or Upward Pressure

General discussion.—The preceding discussion has dealt with stocks that are assumed to have been emplaced effectively by subsidence of columns or blocks. There are a few examples in which subsidence of blocks or columns is inferred to have been the major mechanics of emplacement, but they are also accompanied by evidence of deformation of country rock due to outward side pressure or uplift of roof.

The basaltic lavas around the Mull complex (Bailey *et al.*, 1924, Chapters XII and XIII) show several concentric folds with dips of 10°–30° in discontinuous arcs or circles. Tyrrell's description (1928) of the northern granite mass of the island of Arran, Scotland shows that along one part of the border the country-rock schists have been dragged around by an uplift produced by the granite magma so that their strike swings into approximate parallelism. In another part of the border there has been upward movement by faulting and mylonitization.

Mt. Monadnock, Vermont.—The Mount Monadnock pluton in Vermont is inferred by Chapman (1954) to result from the settling of a domical reservoir which developed cylindrical and radial fractures with consequent cauldron subsidence and stoping of large arcuate-shaped slabs as the major method of emplacement. North and south of the stock, however, quartzites and schists which in general strike about north and dip east have been strongly twisted and their schistosity thrown out of regional strike. Chapman suggests that during the very early stages of intrusion positive magma pressure was sufficiently vigorous for a brief period of time to deform the immediately surrounding metamorphic rocks.

Ahvenisto, Finland.—One of the oldest ring-dike complexes described is the Ahvenisto stock about 17 by 27 km in diameter, in Finland. The following summary is based on the work of Savolahti (1956). The earliest intrusions form an arc and consist of several successive intrusions of gabbro with anorthositic differentiates. The younger gabbro intrusions have chilled contacts against the older. The main core of the complex is a stock of biotitic rapakivi granite. The youngest intrusions are granite porphyry dikes with fine-grained facies in contact with all older rocks. Savolahti (1956, p. 83) writes of the rapakivi granite in general that "At an early period the hypabyssal, partly effusive characters of rapakivis were described. Likewise, the occurrence of miarolitic cavities was recognized to be typical, and the scarcity of aplites and pegmatites was known". The stock is in general discordant to the country rock which consists of migmatites and older microcline granite, but locally the trend of the foliation of the migmatites has been deformed into conformity with the boundary of the intrusive complex. Some of the rapakivi granites in this region have been determined by Kuovo and Gast (1957, p. 30) to be about 1650 million years old, on the basis of Rb-Sr, K-A, and U, Th-Pb.

Other Discordant Plutons of Epizone

Introduction.—The characteristic setting for discordant batholiths associated in space, time, and tectonics with ring dikes, cauldron subsidence, and stocks is a peneplaned surface on a "basement complex" or series of folded and faulted beds overlain unconformably by a veneer of lavas. Such plutons occur in the New Hampshire, Oslo, Nigeria, and Southwest Africa belts and the Glen Coe district that have been referred to. They may be very appropriately called subvolcanic. Although many stocks and batholiths are thus either directly or indirectly associated with cauldron subsidence and ring-dike complexes, many plutons of the epizone are not, although they are in general discordant. Many of these latter plutons are associated with volcanic rocks in space and time, but the evidence is commonly not sufficiently direct to tie both assuredly to the same tectonic history. Some of these plutons may not have had connections that broke through to the surface to yield lava flows. Others probably did have such connections, but the roof either remained intact or broke down and sank in the magma in such a way that direct connection between lavas and the pluton cannot be so confidently inferred as in the case of those

associated with present evidence for caldera subsidence.

The Bayview and Packsaddle Mountain stocks, Idaho, described by Sampson (1928) possibly afford a link between the directly subvolcanic type of pluton and plutons not now associated with volcanic rocks. The stocks are predominantly granodiorite and are significant because probably subsidence of roof rocks has accompanied their emplacement. The stocks are discordant with the relatively flat lying structure of the surrounding rocks, which are predominantly the Precambrian "Belt" series of sedimentary rocks. Block faulting has resulted in downdropping of blocks of Cambrian sedimentary beds. The block faulting is found only about the stocks and is related to the intrusion. The Cambrian rocks are found only where they are more or less engulfed in igneous rock. The granodiorite is coarse-grained up to contacts. The collapse structure recalls that associated with cauldron subsidence. There is no pegmatite in the granodiorite, but there are a few aplite dikes.

An excellent example of control of emplacement of a Precambrian quartz monzonite stock of fractures of the country rock has been described and mapped by Steven (1957, p. 365–375). One border has many *angular* step-like irregularities, and another has a zone 1.5–2 miles wide with a complex network of dikes.

Several stocks or lines of stocks and several batholiths of the epizone will be summarily described. These may be either parallel or discordant to regional structure.

Stocks and volcanic rocks of western Cascade Mountains, Oregon.—The Miocene (?) lavas and the line of Miocene (?) intrusive stocks of the western Cascade Mountain range in Oregon (Callaghan, 1933; Buddington and Callaghan, 1936) afford an excellent example of an association of lavas and plutons of similar composition, and of association in geography and time (fig. 4). The belt about parallels the trends of the substructure. The lavas range from basalt to rhyolite but are characterized by andesite. The intrusive stocks in Oregon occur at intervals along a line about 200 miles in length. They range in size from small plugs to a stock 1½ by 2½ miles in diameter. The rock of the smaller bodies is generally porphyritic aphanitic, that of the largest body is even-grained granular. The rocks range in composition from augite diorite through augite dacite porphyry and augite granodiorite porphyry to granite. The larger masses are in general more siliceous. In the Bohemia district (Buddington and Callaghan, 1936, p. 426) the intrusions occur in an arc and as radial dikes. The line of intrusions has a general northerly trend, but the individual intrusions and veins trend mainly to the west or northwest. Epithermal and xenothermal metalliferous veins are associated with the stocks. An extension of this belt into Washington is shown on the map by Waters (1955, Pl. I).

A belt of Quaternary and late Tertiary volcanoes lies in general to the east and roughly parallel to the line of older Tertiary intrusive stocks.

Snoqualmie batholith, Washington.—The Snoqualmie batholith of Washington (Fig. 4) of early Miocene or late Oligocene age (Grant, 1941, p. 590–593) has been described by Smith and Calkins (1906). It is composed of granodiorite and biotite granite, is miarolitic (Waters, 1955, p. 711), and has porphyritic modifications on the margins of large masses and in dikes. It is emplaced in folded sedimentary beds and in the Keechelus volcanic rocks. The latter are in part gently folded and in part have only initial dips. They consist of pyroxene andesite, dacite, rhyolite, and basalt with the first two greatly preponderating. An analysis of a sample of the andesite shows 18 per cent normative quartz and is very similar in composition to the granodiorite which intrudes it. The batholith is about 10 miles in diameter and is inferred by Smith and Calkins to have consolidated about 4000 feet below the surface. Knopf (1955, p. 695) states that the batholith is roughly 250 square miles in exposed area and may be the top of a mass 4000 square miles in extent not yet uncovered by erosion.

Batholith, Casto quadrangle, Idaho.—The Miocene batholith described by Ross (1934) from the Casto quadrangle, Idaho, is also noteworthy because of its size. It is at least 30 miles long and averages 7 miles wide. Much the most abundant rock according to Ross is granite, but there are small masses of quartz monzonite, granite porphyry, dacite porphyry, quartz diorite, and granophyre. The batholith cuts Oligocene(?) volcanic rocks composed preponderantly of rhyolite and quartz latite, and Ross states that some of the late rhyolitic flows may possibly be related to members of the pluton. The depth of intrusion he infers to have been not much more than 2 miles. The granite is locally finer-grained close to the contact and granite porphyry may be a marginal facies. Micropegmatite occurs in nearly horizontal ribs. The overlying strata were domed into a

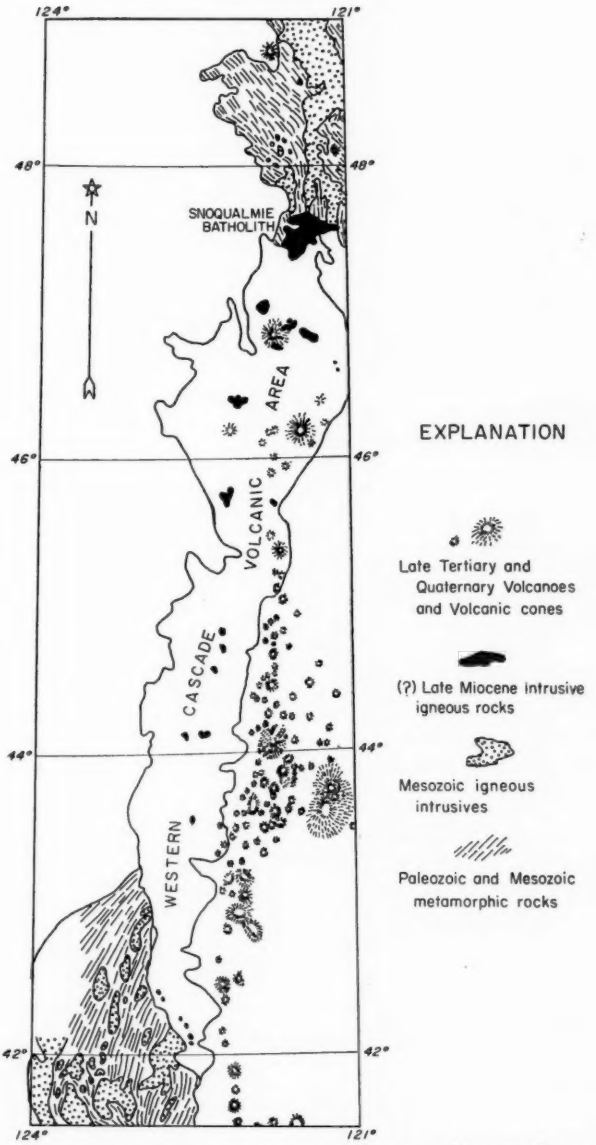


FIGURE 4.—BELT OF TERTIARY INTRUSIVE STOCKS EMPLACED IN VOLCANIC ROCKS OF WESTERN CASCADE MOUNTAINS IN OREGON AND WASHINGTON

Modified after Tectonic Map of United States, Am. Assoc. Petroleum Geologists, 1944

broad low arch by the granite rather than cross-cut. The granite locally has followed faults.

Boulder–San Juan discordant belt of plutons, Colorado.—A series of plutons of Tertiary age occurs in a belt extending from a little northwest of Boulder to the San Juan district in Colorado (Fig. 5), a distance of about 200 miles. The belt is strongly discordant to the regional

structure. Among others it includes the Jamestown, Montezuma, Silverton, and La Plata stocks and the Mount Princeton batholith.

Lovering and Goddard (1950) have described the belt. They state that some stocks probably occupy old volcanic throats, but many others were roofed with pre-Denver (Upper Cretaceous and Paleocene) rocks and probably forced their way in by stoping and intrusive faulting. The earliest intrusives show structure concordant with the country rock much more commonly than do the later, and among the latest of the intrusives explosion breccia is common. Most of the intrusives lie between monzonite and quartz monzonite in composition. The stocks are associated with dikes and sills. The texture in general ranges from coarse porphyritic and medium-grained to porphyritic aphanitic. The intrusion continued intermittently throughout the considerable span of time during which the Laramide revolution was in progress. Local transverse fracture zones marked by intrusive activity followed a period of regional northwesterly folding and faulting. The transverse structure is explained as follows; (Lovering and Goddard, 1950, p. 63).

"As the axis of tension is always perpendicular to the axis of compression and the porphyry belt lies perpendicular to the direction of Laramide compression, it is possible that tensional forces of some magnitude were present here during the folding of the region. The belt of porphyry stocks occupies a position on the northwestern side of a tectonic transition zone between two types of regional deformation. Fault movements in the porphyry belt suggest that the northern part of the transition zone was one of shearing with nearly horizontal movement as well as one of tension. It is believed that these two stresses—shearing and tension—were in part responsible for the rise of the magma that formed the porphyry stocks."

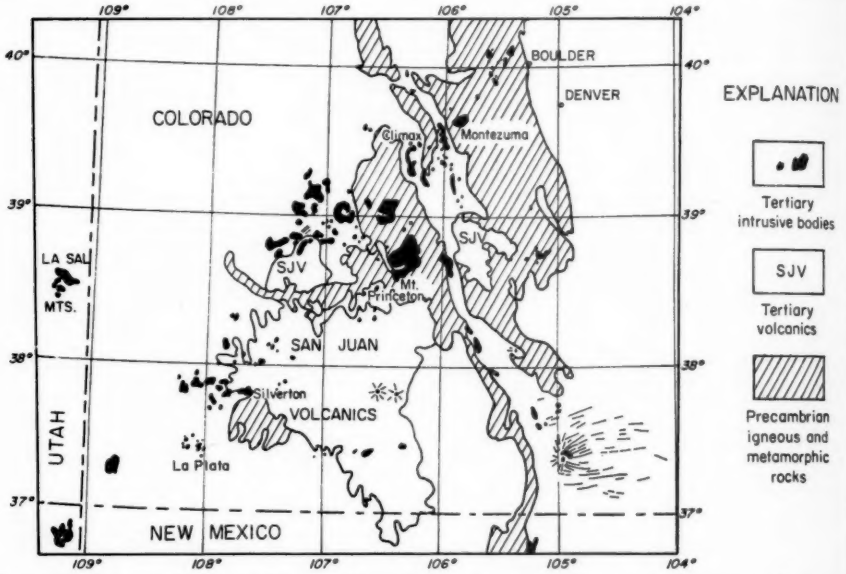


FIGURE 5.—BOULDER-SAN JUAN BELT OF PLUTONS DISCORDANT TO REGIONAL STRUCTURE, COLORADO
Modified after Geologic Map of United States, U. S. Geol. Survey, 1932

Dings and Robinson (1957) have described the Mount Princeton batholith which is one of the largest bodies in the belt. It is about 14 by 19 miles. They describe it as quartz monzonite with small areas of younger granite, intrusive quartz monzonite porphyry, and quartz latite porphyry. Only locally does the rock of the batholith change texture to a porphyry at the border, but apophyses are finer-grained. Small aplite dikes occur throughout. Pegmatite dikes are rare. The younger granite, a leucogranitic type, however, is locally miarolitic and has numerous pegmatite veins. Beryl occurs in the granite, the miarolitic cavities, and the pegmatite. There are two granite stocks, one about 3 miles long and the other 1½ miles long.

The Tertiary Montezuma quartz monzonite stock is an example intruded discordantly in the epizone almost exclusively in Precambrian

significant because the great relief and mine workings permit an accurate picture of their shape and geologic relationships. They are

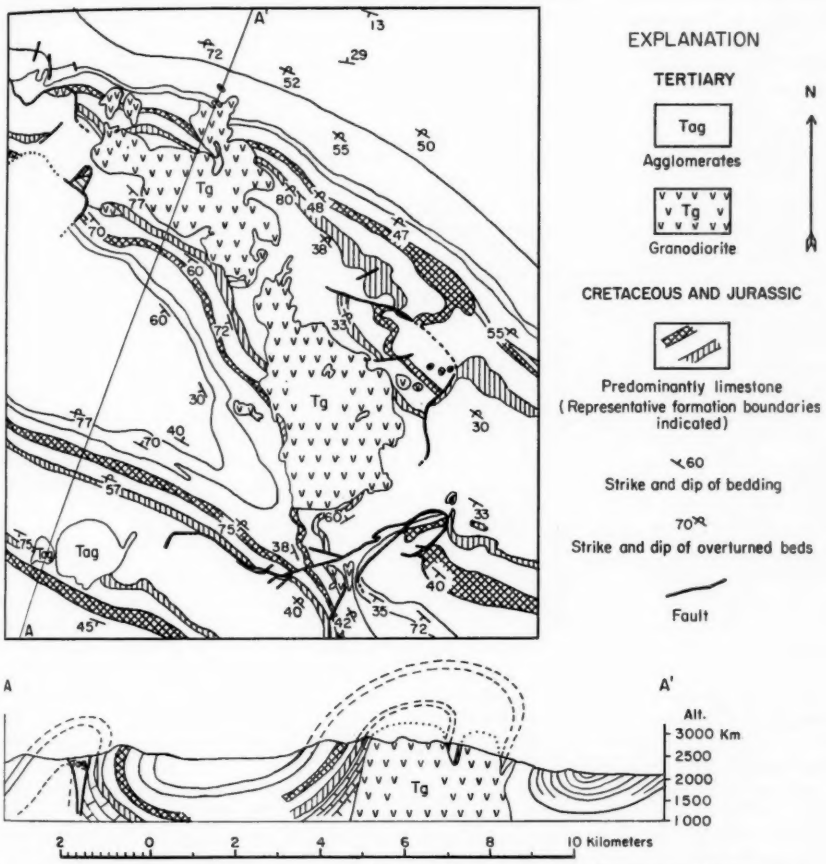


FIGURE 6.—TERTIARY GRANODIORITE STOCKS EMPLACED DISCORDANTLY IN EPIZONE
In asymmetrical anticline of limestone, near Concepcion del Oro, Mexico. After Rogers, Tavera, and Ulloa (1956)

migmatites, schists, and gneisses (Lovering, 1935).

The mineralization and by inference some of the associated plutons of the Boulder–San Juan belt has been stated (Eckelmann and Kulp, 1957) to be 59 ± 5 million years of age.

Stocks of Concepcion del Oro, Mexico.—Two closely adjacent granodiorite stocks of Tertiary age are well exposed northwest of Concepcion del Oro in Mexico (fig. 6). They have been mapped by Rogers, Tavera, and Ulloa (1956) and referred to by Triplett (1952). They are emplaced discordantly in the core of an asymmetrical anticline of Jurassic and Cretaceous sedimentary beds. Limestones are predominant with minor shaly limestone. The roof is faulted in a manner which may be explained as due to a slight doming by upward magma pressure. Roof pendants lead to an inference of a relatively flat archlike roof with re-entrants. The emplacement seems clearly to be due to subsidence of rock from the space now occupied by the stocks. It may also be noted that limestone such as forms the country rock here is generally

considered a "resister" to granitization. The mineral deposits are zoned, in part with a vertical distribution, from hypothermal deposits at lower levels to epithermal chimney deposits in the higher parts of roof.

Boulder batholith, Montana.—A pluton of Late Cretaceous age, of great size for the epizone, and presumably somewhat older than the plutons of the Boulder-Breckenridge belts, is represented by the Boulder batholith in Montana. Knopf (1948, p. 666) states that a great volume of andesite and latite was erupted, probably just before emplacement of the Boulder batholith, which rose to such a high level that it invaded the pile of lavas. Balk (1937, p. 91) states that the Boulder batholith approached the surface somewhere between 2000 feet and 10,000 feet. The batholith is 70 miles long with an area of 1200 square miles. Grout and Balk (1934, p. 880) state that flow structures are poorly developed and (p. 885) that linear structures are much more widespread and uniform, and probably more significant than the foliation as indicating the intrusive movement, although they are also elusive.

Knopf (1957, p. 81) states that the batholith is composite and—that the order of intrusion is (1) basic hypersthene-bearing granodiorite, (2) granodiorite, (3) porphyritic granodiorite, (4) biotite adamellite, and (5) muscovitic biotite granite. Alaskite and aplite are abundant. Contact metamorphism has locally developed sillimanite - cordierite - microperthite hornfels. Knopf describes the emplacement of the batholith as the problem of how five different magmas in turn made room for themselves in the higher level of the crust and built up a composite batholith. He writes that near the batholith the invaded country rock has been more closely folded than at a distance from the contact. In places the strata adjacent to the batholith stand vertically and have even been overturned. Locally a series of reverse faults has developed along the eastern border of the batholith. The intrusive magma according to Knopf has manifestly made room for itself by crowding aside the enveloping rocks, by close appression of the beds, by overturning them, and by imbricate high-angle thrusting.

Knopf reports (p. 90) the age of the batholith as determined by the Larsen zircon method to range from 62–72 m.y. and by the potassium-argon method, 87 m.y.

Seagull batholith, Yukon Territory.—The Seagull batholith in Yukon Territory has been described by Poole (1955), and the following is based on his work. The batholith is about 6 by 28 miles and is emplaced largely in the trough of a syncline of Paleozoic rocks (Fig. 7). The batholith could be of mid-Cretaceous or Late Cretaceous age. It is in a deeply dissected mountain country with great relief and can be shown to have steep walls and relatively flat undulatory roof with several of the mountain peaks capped with hornfels and the valleys in quartz monzonite. The country rocks are regionally metamorphosed and belong to the muscovite-chlorite subfacies. There is no evidence for forceful intrusion or side thrusting. The carbonate rocks have diopside, tremolite, and garnet in the contact zone, at one locality with wollastonite. The rock of the batholith is a coarse-grained leuco-quartz monzonite with flat sheets of fine-grained and porphyritic alaskite. Alaskite in near-horizontal layers up to 20 feet thick forms 5–25 per cent of the mass. There are miarolitic cavities in the quartz monzonite with quartz and tourmaline. Dense spherical aggregates of quartz and tourmaline also occur as replacements in the quartz monzonite and alaskite. There is no pegmatite.

Precambrian Plutons of Epizone

General statement.—The major types of epizonal plutons may be of Precambrian as well as of Tertiary age. Discordant plutons of Precambrian age have been described by Anderson, Scholz, and Strobell (1955) from the Bagdad area, Arizona, and by Kalliokoski from the Weldon Bay area, Manitoba. Other types of Precambrian plutons are referred to below.

Granophyre.—Extensive granophyre sheets associated with gabbroic or diabasic strata-form complexes have been described or redescribed in recent years from the Precambrian of Minnesota (Schwartz and Sandberg, 1940), Wisconsin (Leighton, 1954), the Wichita Mountains of Oklahoma (Hamilton, 1956; Merritt 1958), and the Sudbury complex in Ontario (Thomson, 1956). All these were emplaced in the epizone. Hamilton writes that in the Wichita Mountains, granophyre, granite, and rhyolite form a sheet complex of dozens of separate plutons, of which many are sills and funnel-shaped masses. He states that granite and rhyolite may be either lateral equivalents of granophyre or intercalations in granophyre, and that the granites are probably in general younger than the granophyres. Rhyolite inclusions are abundant in some granophyre. Merritt (1958 p. 33–34) states that miarolitic

EXPLANATION
IGNEOUS ROCKS
(?) Late Cretaceous Seagull batholith, leuco-quartz monzonite and alaskite
(?) Jurassic, (?) Lower Cretaceous, biotite-hornblende quartz monzonite and granodiorite, in part sheared
SEDIMENTARY ROCKS
6 Post-Mississippian, Pre-Cretaceous
4,5 Upper Mississippian and (?) younger; (5) Upper Division, (4) Lower Division
3 Lower (?) and Middle Mississippian
2 Lower and/or Middle (?) Mississippian; (includes some intrusives)
1 Upper Devonian, Lower and Middle (?) Mississippian
Strike and dip of bedding
Fault
0 1 2 3 4 5 MILES
SCALE
N
A

FIGURE 7.—SEAGULL DISCORDANT UPPER CRETACEOUS (?) BATHOLITH, YUKON TERRITORY, EMPLACED IN A SYNCLINE
The quartz monzonite is locally miarolitic. The roof pendants cap the tops of mountains and are underlain by granite. Modified after Poole (1955)

cavities are common in one of the granite masses and that it may have been emplaced as a batholith. A younger granite mass has chilled facies against older rocks. The younger granite is also miarolitic. K/A and Rb/Sr ages of a biotite from the younger granite are reported by Merritt (p. 62) to be 480 m.y. and 500 m.y. respectively.

Thomson (1956, p. 43–45) has proposed that the Sudbury Basin is a volcano-tectonic depression surrounded by a ring complex of dike-like and sill-like character, and that the granophyre (micropegmatite) was emplaced as a ring structure inside the norite.

Ring-dike complexes.—The Ahvenisto pluton of Finland has already been referred to as an example of a Precambrian ring-dike complex. Two other ring-dike complexes, the Chatham–Grenville and Rigaud stocks of probable Precambrian age in Quebec, have been described by Osborne (1934). Chill facies such as quartz porphyry and syenite porphyry are found in both complexes, and miarolitic structure is found in the syenite of the Rigaud stock.

Aureoles of Pseudo-igneous Emplacement

Description.—The contacts of the plutons of cauldron subsidence are almost universally sharp as are the contacts of most other stocks of the epizone. Extensive metasomatism of earlier gabbro members by younger granitic magma, however, has been described by Korn and Martin (1954) from the Messum complex in southwest Africa. The Bingham, Cassia and La Plata plutons in Utah, Idaho and Colorado respectively have been interpreted as cores of magmatic origin with aureoles of pseudo-igneous granite, the product of replacement of quartzite or sandstone. Loughlin and Koschman (1942, p. 41–42) have also described a small body of granophyre interpreted to result from metasomatism of sandstone by emanations from an adjacent Tertiary granite body.

Bingham, Utah, stock.—Stringham (1953) has described a small stock at Bingham, Utah, where granite forms about two-thirds of the area of the pluton and is inferred to be the product of granitization of quartzite. Some of this granite is exceptionally high in K_2O. The core of the stock is granite porphyry which is interpreted to be of magmatic origin. In the area to the south (Gilluly, 1932, p. 65) a series of volcanic flows in which latite is overwhelmingly predominant are cut by intrusives inferred to be roughly correlated with the Bingham stock and to be of late Eocene or Oligocene age.

Cassia batholith, Idaho.—Anderson (1934) has described the present 60 square miles exposure of the Cassia batholith to consist of about two-thirds porphyritic, usually gneissic granite and one-third granodiorite. He believes the porphyritic granite gneiss is a replacement of metaquartzite and the granodiorite a crystallized magma. The batholith has a dome-shaped roof, and the metasomatic porphyritic granite extends at least 1800 feet down. The batholith is of late Cretaceous or early Tertiary age. The data are not too definitive, but the batholith is here classified as emplaced in the epizone.

La Plata stocks, Colorado.—Eckel (1949) has inferred the emplacement of small Late Cretaceous or Tertiary diorite and monzonite stocks in the La Plata District, Colorado (Fig. 5) to be in part by replacement or assimilation of country rock. He finds (p. 39) that where a monzonite stock transects beds of sandstone there are inclusions from an inch to several hundred feet in length which retain the attitude and position of the beds from which they were derived. However, he also finds that in many places contacts between the diorite and monzonite and the host rock are sharp and that the diorite and monzonite locally contain fragments of Precambrian rocks even where they are in Paleozoic or younger sedimentary beds.

Supplementary Descriptions of Plutons Emplaced in the Epizone

New Cornelia quartz monzonite stock, Arizona.—The New Cornelia quartz monzonite stock in the Ajo district of Arizona exhibits many features characteristic of the Tertiary stocks of the southwestern United States. The following description of it is condensed from that by Gilluly (1946).

The great copper mine at Ajo is opened in a low-grade epithermal deposit of chalcopyrite and bornite disseminated in the New Cornelia quartz monzonite that is tentatively referred to Early Tertiary age. The New Cornelia stock is exposed over an area of about 6 square miles. There is a discontinuous border facies consisting of fine-grained quartz diorite. The preponderant rock is an equigranular quartz monzonite with a poorly developed linear structure. The country rock is predominantly the Concentrator volcanic rocks consisting of andesite, keratophyre, and quartz keratophyre flows, breccias, and tuffs with highly altered and complex structure. The Cornelia intrusion Gilluly infers probably took place under a moderate

cover of rocks after folding and perhaps faulting of the Concentrator volcanic rocks (Cretaceous ?). He states that it is possible that the Cornelia quartz monzonite and Concentrator volcanic rocks represent the same magmatic cycle. The disregard of older structures by the intrusive, the absence of wall-rock structures concordant with its contacts, and the sporadic preservation of fine-grained (chilled) border facies indicate that the intrusion took place at a relatively shallow depth. The weakness of lineation in the rock is inferred by Gilluly to indicate that there was little motion in the magma at late stages of its consolidation. After its consolidation, however, it was fractured along westward-trending fissures, and aplite dikes were injected in large quantities. Northward-trending fractures followed and were occupied by pegmatites in the apical part of the stock. At later stages solutions chloritized and sericitized the rocks of the apical part of the stock and deposited cupriferous and associated metallic minerals of the New Cornelia ore body.

Hanover stock, New Mexico.—The Hanover granodiorite stock, New Mexico, has been described by Paige (1916), Schmitt (1933), and Kerr *et al.* (1950). Where emplacement has been accompanied by uplift and outward deformation. It is about 2.5 miles long, north to south, and less than a mile wide. The Paleozoic bedded rocks dip away from the stock on the east and west flanks so that it has the relationship of an anticlinal structure. At the south the bedded rocks have been deformed into an overturned syncline and an asymmetrical anticline beyond. The fold axes form arcs parallel to the edge of the stock as though the folds had been formed by lateral pressure from the overriding stock. Locally folding was so intense that thrusting occurred on a low-angle fault plane. Kerr *et al.* (1950, p. 301–302) state that the near-by Santa Rita stock arched and cut through overlying sedimentary rocks and quartz diorite sills.

Marysville stock, Montana.—The development by Barrell (1907) of the hypothesis of block subsidence in magma as the mechanism of emplacement of the Marysville granodiorite stock has made the latter one of the classic examples of this phenomenon. Knopf (1950) writes that the stock is 6 miles north of the northern end of the Boulder batholith and probably an outlying cupola. It is only 3 square miles in area. Barrell states that the roof sediments were domed over the granodiorite to the extent of 1000 feet, possibly 3000 feet; that faulting immediately preceded the invasion of the stock caused by upward pressure of the igneous mass; and that at numerous places the roof of the stock passes beneath the sedimentary cover at a flat angle. Barrell further writes that the granodiorite maintains granularity up to the contact and is medium- to coarse-grained but becomes markedly more porphyritic in outlying tongues and wedges. Aplite occurs within the margin of the stock and in rocks of the border zone but is rare in the interior. There is also minor pegmatite in the same zones as the aplite. Knopf comments (5950, p. 840–842) on the remarkable contact-metamorphic aureole. The argillites are converted to cordierite hornfels, and the limestone to diopsidic and tremolitic hornfels.

Organ Mountain batholith, New Mexico.—A small discordant Tertiary batholith of about 55 square miles in area has been described by Dunham (1935) from the Organ Mountains of New Mexico. He infers that Tertiary andesite flows form the roof for the intrusive comparable with the roof of a laccolith and that in depth the body is crosscutting with steep outward dips and was emplaced by piecemeal stoping. There is evidence that some xenoliths have sunk not less than 1400 feet and probably much more. The dip of the andesite roof is away from the batholith, exceeds 50°, and swings around with the contact. Locally the wall rocks have been powerfully distorted by magmatic pressure. The batholith is composite and consists of three distinct bodies, a monzonite, quartz monzonite and quartz-bearing monzonite. The quartz monzonite has tiny miarolitic cavities as a widespread feature of a porphyritic fine-grained facies. The intrusive process according to Dunham was accompanied by a progressive concentration of volatile fluxes. There are no pegmatites or aplites in the monzonite; aplites but no pegmatites in the quartz monzonite (17.5 per cent normative quartz) and aplites, pegmatites, and mineral veins in the quartz-bearing monzonite (10 per cent normative quartz). The aplites are very small dikes and veinlets. Quartz porphyry sills and dikes occur in the country rock (Dunham, 1935, p. 84). Wollastonite (p. 100) has been formed locally in the limestone contact with the late intrusions.

Paleozoic leucogranite and granite porphyry batholiths, Newfoundland.—Two examples of Paleozoic miarolitic leucogranite or alaskite batholiths emplaced in the epizone have been described by White (1940) and by Van Alstine (1948), both from the south coast of Newfound-

land. The roofs of the batholiths are relatively flat, in part covered with roof pendants, and have gently outward dipping walls. The granite is miarolitic and homophanous. Chilled contacts are rare but were observed. The St. Lawrence batholith (Van Alstine, 1948) of Devonian (?) age has related rhyolite porphyry dikes in the country rock and epithermal fluorite deposits. It is elongated in a direction approximately normal to the trend of the major folds and thrust faults of the Cambrian and Ordovician (?) rocks and is inferred by Van Alstine to have been emplaced by stoping. The Ackeley batholith (White, 1940, p. 969) is believed to occupy more than 300 square miles. A miarolitic alaskite facies is associated with molybdenite and muscovite metasomatism. Locally where the batholith is bordered by volcanic rocks there is an agmatite zone 3 miles wide.

Another discordant Devonian (?) batholith of the epizone has been described from the north coast of Newfoundland by Snelgrove (1931, p. 24–25), Baird (1951, p. 49–52), and Neale (1957). The batholith occupies at least 75 square miles in area southwest of Confusion Bay, west of Notre Dame Bay. The rock is described as a granite porphyry or quartz porphyry. Foliation and lineation are marked in marginal facies. Many inclusions of Devonian (?) rhyolitic volcanic rocks occur locally in the border facies. Neale (1957, p. 59) suggests that the volcanic rocks and the prophyry are intimately related, and all the authors infer shallow intrusion. So large a batholith of granite porphyry is very unusual, and it deserves additional detailed study.

Plutons of Transitional(?) Epizone–Mesozone

Introduction

There are several batholiths whose description suggests characters appropriate in part for the epizone and in part for the mesozone. They are therefore here included in a transitional (?) group until more definitive classification can be made. The Texas Creek granodiorite batholith (Buddington, 1929a), a unit of the Coast Range intrusives of Southeastern Alaska, is representative of the kind of problem involved. The batholith has a sharply discordant broad relatively flat roof, common aplite and pegmatite dikes in the contact zones only, and associated porphyritic aphanitic dikes. These features ally it with the epizone. On the other hand it has a foliation throughout and is emplaced in close-folded country rocks—characters appropriate for the mesozone.

Examples of plutons with transitional characteristics appear to be not uncommon in Europe. Several late Hercynian granite complexes in Portugal described by Westerveld (1955) are post-tectonic and almost wholly discordant, but also have steeply dipping planar foliation in substantial part parallel to the borders of the pluton, but locally at an angle.

Southern California Batholith

The huge batholith of Southern California displays predominant discordant contacts and certain other features which ally it with plutons of the epizone, whereas the near absence of chill zones, and the occurrence of internal border foliation and local concordance of structure of country rock to contacts tie it to batholiths of the mesozone.

The northern part of the batholith of Southern California has been described by Larsen (1948), from whose work the following summary is made. The batholith is exposed for a length of 350 miles and a width of about 60 miles. It has a length of probably over 1000 miles if discontinuous bodies at the southern end are included. The batholith was intruded in early Late Cretaceous time. In the area studied by Larsen the batholith was emplaced by more than 20 separate injections. The country rocks were regionally closely folded, metamorphosed, and intruded by earlier granitic rocks, perhaps in late Paleozoic and Triassic sediments, the orientation of the inclusions and other structures of the batholith, the elongation of the batholith, and the strike of the major faults are in about the same direction. Larsen infers that the batholith was emplaced by stoping and not by forceful injection. Forcing apart of the walls may have been important in furnishing room for some of the elongate members of the batholith, but it could not have furnished a large part of the space for the batholith as a whole. He concludes that there is no relation between proximity to granitic bodies and degree of metamorphism, except for local contact metamorphism and for thin screens between intrusive masses and small inclusions. For the most part there is little contact metamorphism where the granitic rocks intrude large bodies of older schists, slates, and quartzites. Some of the screens and inclusions in the granitic rocks, however, have been greatly metamorphosed.

The slates were changed to mica schists and to injection schists, the quartzites to mica-garnet-quartz rocks or to quartz-sillimanite rocks. Local bodies of marble around tonalite have been replaced by garnet, diopside, wollastonite, idocrase, feldspar, etc. Many of the intrusive bodies have zones next to their contacts that are banded or gneissoid. Gabbro forms about 7 per cent of the batholith, tonalite 63 per cent, granodiorite 28 per cent, and granite 2 per cent. Larsen is of the opinion that in the area described the rocks had only a moderate temperature when the first member, the San Marcos gabbro, was intruded, as small bodies of that rock are rather fine-grained. Locally aplite dikes are miarolitic. Larsen does not discuss the possible depth at which the present level of the Southern California batholith was emplaced but states (1945, p. 404) that it was probably intruded to within a few kilometers of the surface. Chayes (1956) is of the opinion that the tonalitic rocks are the product of a mechanical mixture and interaction between granodioritic magma with previously solidified gabbro. In most places contacts of the intrusive bodies are sharp. Chilled borders were not found except in one granodiorite dike. Merriam (1946) describes concordance of structure of country rock with batholith contacts in the Ramona quadrangle.

Batholith of Southwestern Nova Scotia

The geology of the great batholith of southwestern Nova Scotia (Fig. 8) has been summarized by Wright (1931). It is more than 110 miles long, 20–30 miles wide, and together with satellitic bodies has an area of 4000 square miles. The eastern part consists of biotite and muscovite granite that rarely shows gneissoid or banded structure. Aplitic and pegmatitic facies are common, and the texture of the granite is maintained up to the contacts. The contacts are sharp. Andalusite hornfels has locally been formed in adjoining slate. The country rocks are predominantly folded late Precambrian chloritic and carbonaceous slate and sandstone. The beds are in broad folds which are transected by the batholith, without appreciable distortion or deflection. The invading magma is inferred by Wright to have displaced its host without appreciable lateral thrusting or doming of the roof. Mesothermal gold-quartz veins occur in the country rocks. Wright quotes Fairbault as estimating that 9 miles of the Precambrian Goldenville formation had been eroded, mostly before Mississippian time. Locally the batholith is reported to cut fossiliferous beds of Silurian and Devonian age. Most of the data of Fairbairn (1957), however, based on rubidium-strontium ages of mica suggest ages of between 350 and 400 million years, or between Middle and Late Ordovician. These discrepancies in ages are at present unresolved. The characters of the batholith seem to be definitely those of the epizone, but it is not certain what significance is to be drawn from Wright's reference to 9 miles of eroded material. The axis of the batholith is in part strongly discordant to the fold axes of the regional structure. The discordant Boulder–San Juan (Colorado) line of plutons, described earlier, may be referred to as a much "nearer-surface" expression of similar relationship.

Plutons of Mesozone

"The granite was once hot, full of gas and molten . . . it rose along a large broad front, stretched out and expanded sideways and yielded to a force from the depth which pushed and drove it." Hans Cloos, 1953.

Introduction

It may be expected that a substantial period of time would be necessary to permit erosion to expose plutons of the mesozone. The fact that no plutons of Tertiary age in North America are known to the writer to be emplaced in the mesozone is consistent with the foregoing principle. In the western Cordillera, Jurassic to Lower Cretaceous plutons, however, are dominantly of mesozonal character.

Characteristics

The individual plutons of the mesozone are inferred normally to have the following characteristics. The degree of metamorphism of the regional country rock is not more intense than the green-schist and epidote-amphibolite facies. The argillaceous country rocks of sedimentary origin are usually slates and phyllites. The inferred temperature of the country rock at the time of intrusion is generally no higher than 400°–500°C. There is no apparent direct relationship between the plutons and volcanic rocks. The stocks and batholiths are effectively always of composite character made up of two or more units. The units in general vary systematically; the younger intrusions are more alkalic and siliceous. The characteristic plutons have *complex* emplacement relationships to the

country rock—*in part discordant, in part concordant.* Locally there may be some replacement. Some may show transection of roof in

ally, gentle dips in the core or parts of the co
may indicate a domal roof. The planar structu
of some plutons may suggest a rough funn

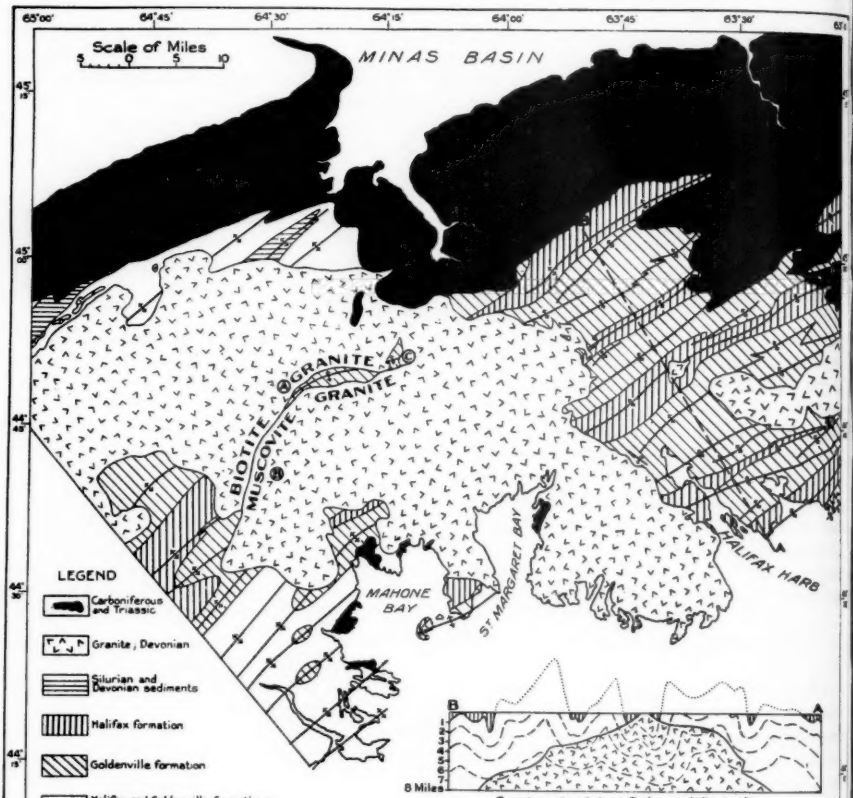


FIGURE 8.—GREAT DISCORDANT DEVONIAN (?) GRANITE BATHOLITH OF SOUTHWEST NOVA SCOTIA
Emplaced in lower part of epizone or upper part (?) of mesozone. After W. J. Wright (1931, modified after E. R. Fairbault)

archlike shape, and have steep outward flaring walls in depth. Rarely, a mass such as the Sugar Hill pluton in Vermont (Doll, 1951, p. 44) has crowded a series of uniformly north-northeast trending metasediments into a conformable steep dipping funnel. Planar foliation is often well developed, especially in the outer portions of the pluton, but commonly is local, elusive, or missing in the core. The planar structure of characteristic batholiths and stocks, especially in the border zones, is subvertical, consistent with vertical upward flow of magma. Occasion-

structure either right side up or upside down with the axis vertical or at moderate inclinations; often the structure may be as shown in Figure 9. Younger units may crosscut the foliation of older units, or locally the planar flow structure may be independent of boundaries of units within a composite pluton (Fig. 9) and maintain its swing across their contacts. The planar structure in some plutons is in part systematically oriented at an angle to the outer border of the pluton. Linear structure may occur in the planes of the foliation or in parts of

the core of the pluton without planar structure. Assimilation may be significant in border or roof zones. Wall rocks in the contact zones often show the development of a steep schistosity conformable with the contact and with a linear structure more or less parallel to the dip, indicating flowage in a subvertical direction. Uplift of the roof may be inferred. Minor fold axes and lineation of country rock adjacent to the pluton may have steeper plunges than further away (Trefethen, 1944, Pl. 1). Bedded rocks or dikes at large angles to the contact may be crumpled back on themselves as though deformed by outward pressure from the pluton. Bedded rocks or older sills parallel to the contact may show boundinage structure due to distention.

Emplacement by reconstitution and replacement of country rock is commonly either absent or subordinate. An occasional small pluton, however, may be emplaced wholly by replacement. Chill-border facies, in the sense of aphanitic texture, are absent. Typical migmatites are commonly minor and are often absent. Pegmatites and aplites, however, may be common, especially in border zones. They may have a radial fabric in some plutons. Miarolitic structure is absent. Marginal fissures with inward dips, in part lined with aplite or pegmatite, may be present locally in border zones of plutons. The plutons are pre-eminently those where the applicability of Cloos' system of "granite tectonics" is most rewarding.

Some batholiths may be bordered by a zone of dike injection or contact agmatites. Dikes (Fig. 13) or dike systems (Pl. 1) as well as sills may occur in the country rocks bordering the intrusives. Hutchinson (1955) has shown that in the Ross Lake area, Northwest Territories, Canada, pegmatite veins of an area of several square miles are spatially related to a body of granodiorite. In the hottest zone near the granite they are often large and emplaced by granitization of granodiorite layers whereas in a cooler zone they were emplaced as pegmatitic fluids along dilatant fracture zones, in part with the development of zoning of the "complex" type of pegmatite.

Contact-metamorphic aureoles may be well developed around stocks (Philbrick, 1936; Pitcher and Sinha, 1958) and small batholiths and around areas of dike complexes in roof zones (Eric and Dennis, 1958, Pl. 1). In the larger or relatively deep mesozonal batholiths regional metamorphism is associated. Phyllites and slates are changed to high-grade crystalline schists, and hornfels may form from metavolcanic rocks or metalimestones in the vicinity of contacts. A schistose structure is common in the country rock bordering mesozonal plutons.

Mesozoic Plutons with Both Discordant and Concordant Relations to Country Rock

White Creek batholith, British Columbia.—A late Mesozoic batholith described by Reesor (1954), from British Columbia shows clearly many significant phenomena (Fig. 9). The country rock consists of the Proterozoic Lower Purcell series regionally recrystallized to phyllites, little deformed in the eastern part of the area but compressed into isoclinal folds in the western part. The rocks belong to the greenschist metamorphic facies. The batholith is about 12 to 17 miles in diameter. There is a contact-metamorphic aureole of about 1000 feet diameter, and all the rocks of the contact zone are schistose. The batholith crosscuts a north-plunging anticline of Proterozoic rocks. Although the batholith in part truncates preexisting structures, the bordering strata are generally visibly and violently side-thrust and forced to conform with the direction of the contact. Vertical isoclinal folds occur along the north and south borders. In one area a marked cross cleavage has developed; fracture cleavage has developed in competent beds, crenulations with cleavage parallel to axial plane in phyllites, and a planar foliation across the bedding. A vertical upward motion of the magma during emplacement is indicated by the vertical to near-vertical lineation and by joints. Evidence of stoping is indicated by an almost universal irregularity of the contact of the pluton with country rock and by local stoping. Inclusions occur everywhere in varying amounts, except within the interior granite. The rocks of the batholith consist, in order of their emplacement, of biotite granodiorite, hornblende granodiorite, and porphyritic granodiorite in roughly concentric arrangement with an elongate core of quartz monzonite. The quartz monzonite grades into an aplitic facies which cuts the other rocks. Aplites and pegmatites occur in great abundance in parts of the mass, notably in the porphyritic granodiorite but not in the quartz monzonite. Inward-dipping joints are well developed throughout the batholith, and many are filled with aplite or pegmatite. They rarely extend into the sediments. The forceful emplacement of the pegmatite and aplite by dilation is well shown. They are

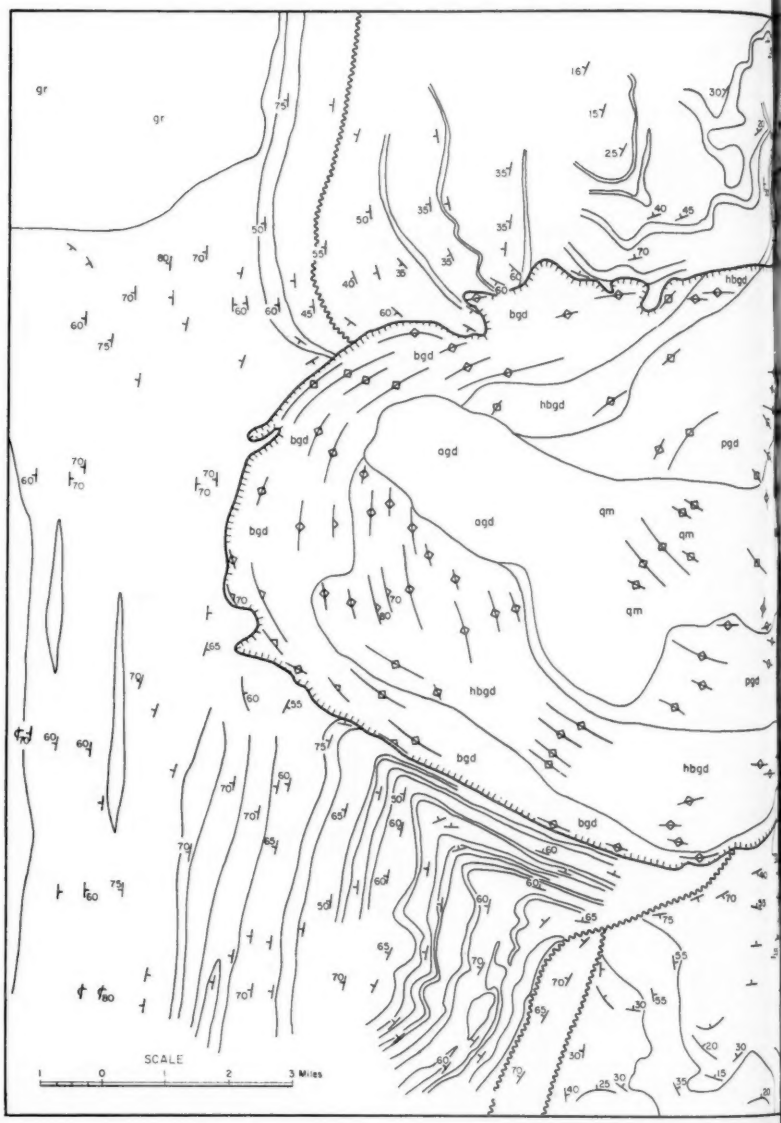
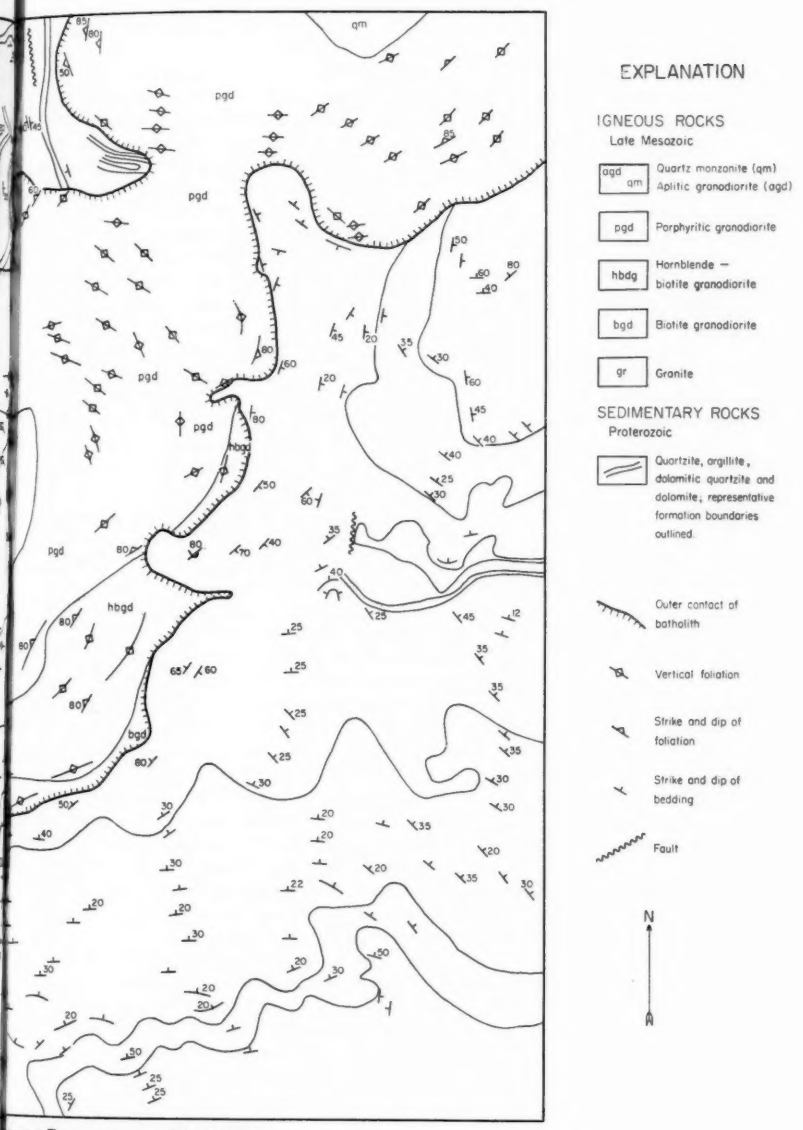


FIGURE 9.—REPRESENTATIVE C[ontact] OZOIC [R]
In part discordant, in part concordant because of crowding aside of country [rock] e Cree

inferred to have originated at the last stage in consolidation of the interior granite. The interior planar foliation is universally vertical to subvertical, and although generally conformable to the shape of the batholith it locally crosses the boundaries between units, and locally at the border contact of the complex it follows every irregularity. There is no linear structure in the quartz monzonite. A mafic-rich facies of the granodiorite may be due to incorporation as indicated by the presence of basic inclusions.



ozoic Batholith of Mesozone
e Creek batholith, British Columbia. Modified after J. E. Reesor (1954)

Sierra Nevada batholith, California.—The Sierra Nevada pluton is about 300 miles long and 50–60 miles wide. It has not been fully explored, and an adequate systematic unified description of the existing data is not available. Calkins (1930) has published a geologic map of the Yosemite area, and Cloos (1936) has published a structural study of the batholith of Yosemite National Park and vicinity and of an area northwest of Lake Tahoe. The structural study has been effectively summarized by Balk (1937, p. 65–67). Only some pertinent ideas

from literature later than that available to Balk will be cited here.

Hamilton (1956, p. 21–23) has given a summary upon which the following abstract is based. The granites were intruded in hundreds of separate plutons, some a few acres in extent and some covering several hundred square miles. Contacts are sharp, and gradation from granite to country rock commonly takes place in less than an inch. The uniformity of the granitic rocks over wide areas, and the gradual nature of the variations indicate that large volumes of the material could be mixed and homogenized. Some of the intrusive material seems to have been wholly liquid (as in the alaskites), whereas some was only partly liquid.

The granites intruded and produced contact metamorphism of a country rock which had already undergone moderate regional metamorphism. Structures in the metamorphic rocks are cut across sharply by the granites, and straight dilation dikes from the granites transect contorted metamorphic rocks. It is possible, however, that some of the deformation of the country rocks was the result of forces of intrusion acting before establishment of the final contacts. Early plutons intruded the metamorphic rocks; later plutons intruded earlier plutons.

The intrusive granites moved generally upward, as shown by their flow structures. Hamilton states that stoping operated, but to a degree that is only conjectural. He infers that an explanation in terms of cauldron subsidence–stoping on a huge scale could account for the emplacement of some of the plutons, particularly the smaller ones which are intrusive entirely into other plutons. However, he finds that no evidence for such emplacement has been recognized in the Sierra except that the geometry of some contacts might favor it. His conclusion is that the plutons formed from mobile magmas which moved upward and expanded outward, mostly passively but in part forcibly. Large amounts of material were incorporated into the margins by assimilation of wall rock and stoped blocks, but most of the granitic material was introduced from lower levels.

Durrell (1940), Macdonald (1941), and Mayo (1941), who have studied contact relations in the Sierra, have concluded that, whatever the means of intrusion, these means were passive. They find that contacts are mostly complexly discordant in detail and, if the wall rocks were shouldered aside, it was apparently accomplished with shearing distributed through broad zones about the intrusions, not with shearing along the contacts.

Mayo (1941, p. 1081) suggested that the dominant means of emplacement of Sierra plutons was "permissive intrusion, tectonically controlled," and "the structural features of the region seem in harmony with the idea that space for the intrusion was provided . . . mostly by buckling of the isoclinally folded wall rocks as a result of a north-south compression".

Durrell (1940) and Macdonald (1941) believe that the belts of country rocks within the batholith are roof pendants with relatively flat bases, remaining portions of a once-continuous roof. They agree that the contacts of the igneous bodies dip outward in most places 60°–70° and that there is a suggestion that the upper parts of the stocks, and probably all the larger intrusives, are more or less dome-shaped. Balk (1937, p. 67), on the basis of the work of Cloos, states that an eastern pluton of the batholith in the Yosemite region has what might be called a schlieren dome were it not for a small mass of structureless granite at the core, and that "each schlieren dome, or arch, is composed of a number of closely related, but petrographically different, rock types which tend to conform with the dome structure, as a system of concentric shells". This pluton also shows marginal upthrusts along the contacts of the oldest intrusion. A comparison of the geologic map by Calkins (1930) and the structure map of Cloos suggests that the flow structure in part crosses the boundary of units as in the White Creek batholith, British Columbia. The foregoing discussion deals largely with the central part of the batholith. Webb (1938, p. 315) finds that in the southern more deeply eroded part of the batholith the foliation of the septae have high-angle dips, none less than 60°.

Coast Range batholith, Alaska–British Columbia.—The upper Jurassic to Lower Cretaceous Coast Range batholith of Alaska and British Columbia has a length of at least 1250 miles with widths of 35 to 60 miles common and up to a maximum of 125 miles. A substantial part of the batholith consists of screens of schist and gneiss. There are few detailed maps of any parts of the batholith.

The batholith in a general way parallels the trend of the prebatholithic structures, but only in a general way. Phemister (1945, p. 79) notes that near Vancouver, British Columbia, "The country rocks strike slightly north of east, while the batholith has its greatest extension from south to north". Buddington (1929, p. 293) describes part of the west border of the bath-

olith as extending for many miles parallel to the strike of the adjacent formations, although locally crosscutting; he notes that for a length of 40 miles the batholithic margin strikes nearly north and transects the general structure at an angle of 15° to 40° whereas the northern part trends northwest at a slightly greater angle than the formations of the country rock. The batholith is stated to work across a synclinorium of Mesozoic rocks into Carboniferous rocks.

Smith and Stevenson (1955, p. 816–817) write concerning the emplacement of the intrusives in southern British Columbia that in many places the batholiths transect the structures of the country rock, that in some places much of the rock was pushed aside, and that trend lines around the southern end of the Coast Range batholith were probably formed by broad-scale and strong lateral pressures transmitted through the magma. The formations southwest of the batholith in southeastern Alaska are generally isoclinally overturned to the southwest, and their dip and the dip of the foliation of the border belt of the batholith is steep northeast or vertical.

Also in southeastern Alaska (Buddington, 1929, p. 181) reconnaissance indicates that the quartz diorite is predominant in the southwestern part (5 to 15 miles wide) of the batholith, and quartz monzonite is predominant in the eastern part (10–15 miles wide) with mixed rocks of generally granodioritic character in the core. Smith and Stevenson (1955, p. 811) describe the igneous intrusions in southern British Columbia as consisting of dioritic to granodioritic rocks in the western portion on Vancouver Island, predominantly granodiorite in the Coast Range, and principally granitic in central and eastern British Columbia. The foregoing relationships recall the Sierra Nevada batholith about which Durrell (1940, p. 12–13) writes that by far the most abundant plutonic rock in the area studied by him (southwestern part of batholith) is quartz diorite but that the most easterly plutonic rocks are quartz monzonite and granite, and that there is a gradual, although overlapping, progression from basic types in the west to acid types in the east.

The batholith is exposed along Tracy Arm in southeastern Alaska for a width of about 15 miles at an angle of 60° to the trend of the major structure. The intrusive rocks contain many large belts of injection gneiss and so many inclusions of country rock that it is doubtful if any area as much as 10 feet square is clear of them (Buddington, 1929, p. 69).

The satellitic intrusions and the northern part of the Coast Range batholith in southeastern Alaska have characteristics definitely like those of bodies emplaced in the mesozone; the southwestern part of the main batholith and the adjoining country rock equally definitely have characters like those of the catazone. The northeastern part of the batholith appears to belong to the upper part of the mesozone or even the lower part of the epizone. A difference in degree of metamorphism of the country rock bordering the western and eastern parts of the batholith was early recognized by the Wright brothers (Wright, F. E. and C. W., 1908, p. 67) and discussed later by Schofield (*in* Schofield and Hanson, 1922, p. 65–66) and by Buddington (1928, p. 293–294). The batholith in southeastern Alaska is bordered on the southwest by a belt of medium- to high-grade metamorphic rocks. This belt has a width of about 35 miles at the southern border of Alaska; it narrows and pinches out at the north near Juneau. The belt of metamorphic rocks changes in metamorphic intensity toward the batholith from the general regional green-schist facies on the southwest through garnet-biotite and staurolite-kyanite zones to a sillimanitic facies with a migmatite zone adjacent to the batholith. There are many plutons of granodiorite or quartz diorite throughout. The rocks to the northwest along the southwest border of the batholith and along the northeast border of the batholith are slates and greenstones. It might be suggested that the belt of medium- to high-grade metamorphic rocks on the southwest border overlies an extension of the main batholith at depth and that the overlying schists were forced up from deeper zones by the upward push of underlying magma and by the accentuated upward drag of the magma mass which formed the southwestern part of the main batholith. The mechanism suggested resembles, but on a larger scale, the idea of upward drag or upward thrust of walls by rising magma proposed by Noble, Harder, and Slaughter (1949, Fig. 4). The quartz monzonite and granitic rocks of the eastern part of the batholith are younger than the quartz diorite of the western part. Granodiorite porphyry dikes of a character appropriate for the epizone are abundant locally in the country rock of the eastern border and are inferred to be related to the quartz monzonite.

Mesozoic Pseudo-igneous Plutons or Facies of Mesozone

Swedes Flat pluton, California.—Two examples of plutons interpreted by their describers

as emplaced by recrystallization and replacement in the mesozone are the Swedes Flat stock in California and the Chilliwack batholith in Washington. The roof (Pellisier granite) of the Inyo batholith, California, has also been interpreted as a product of recrystallization and replacement.

Compton (1955) has described the Swedes Flat pluton and interpreted it as the product of recrystallization and replacement. The main mass of the pluton is about 5 by 7.5 miles in diameter. Tonalite and granodiorite form the preponderant bulk of the pluton with about 4 square miles of gabbroic and dioritic rocks at the north end and another mass at the south end. Granophyre forms a local late intrusive phase. Gradational contacts between granodiorite and dark hornfels and amphibolite are striking. The latter give way to homogeneous granodiorite through a broad zone of intricately veined mixed rocks, 100–1000 feet wide against gabbro and diorite, up to 3 miles wide against metavolcanic rocks. The regular, gradational changes from the incipient webbing of these mixed rocks to inclusion-charged granitic rocks and then to granitic rocks with only vague hornblende clots suggest that the granitic rocks have passed through these stages in their development. Compton believes that a replacement origin for the homogeneous rocks is supported by their lack of flow structures or fracture pattern and by the fact that the foliate inclusions fit the projection of country-rock foliation through the pluton rather than any reasonable movement picture within it. He suggests that most of the granitization was produced by fluids moving in open channels and that the source of these fluids was probably a magma that formed the core of Swedes Flat pluton. Such a magma he infers would have lain south of, and perhaps at a lower level than, the rocks as now exposed.

Pellisier granite facies of Inyo batholith, California.—The Pellisier granite facies of the Inyo batholith, California, of middle or late Mesozoic age has been interpreted by Anderson (1937) as a roof facies of a major batholith developed *in situ* by replacement and recrystallization of both sedimentary and igneous rocks. The granite carries abundant inclusions, most of which appear to have originally been schistose or argillaceous. The replacement origin he bases upon field evidence of gradation between country rock and granite, the variability in composition of the granite, the inheritance of a structure closely resembling stratification, and the microscopic evidence of successive replacements, especially albitization. The part of the batholith mapped is 35 miles long. The Pellisier granite is in substantial part a hornblendic granite, whereas the main part of the batholith is a biotite granite. The solutions effecting the development of the Pellisier granite are inferred by Anderson to have been derived from the underlying magma which crystallized to form the main part of the batholith. Migmatitic gneisses have been formed in the border rocks of the batholith at depth.

Chilliwack batholith, Washington.—The description by Misch (1952) of the Chilliwack batholith, Washington, affords an example in which the hypothesis of granitization has been applied to explain the development of a batholith in the mesozone in the latter part of the Mesozoic. The batholith is about 35 miles long and 5–10 miles wide in Washington and extends north into British Columbia. The country rocks are a series of geosynclinal rocks, mostly phyllites, quartzites, marbles, greenstones, and greenschists except at the southern end of the batholith where, in the border zone of the batholith, the phyllites are changed to mica schist, and the greenstones and green schists to amphibolites. The granodiorite and quartz diorite of the batholith are inferred by Misch to be the result of a continued granitization process which first yields a series of granitic gneisses (the Skagit gneiss) and then large directionless granite bodies with gradual passages between. The country rocks on this hypothesis are not pushed aside along part of the contact, but in part the granodiorite is reported to have moved as a plastic crystalline mass and intruded the metamorphic rocks. Several smaller bodies appear as isolated intrusive stocks which have forced their way by pushing the metamorphic rocks aside. Part of these intrusives are in Lower Cretaceous rocks. The magma of these intrusions is assumed by Misch to have formed at depths below the level now exposed as the final climax in a long process of granitization and mobilization, and it is stated that it did not come from far away or an unknown depth. The depth of formation of the granitic gneisses and granites he estimates at three or four to ten miles.

Mesozoic Plutons with Protoclastic or Late-Stage Postconsolidation Deformation

Colville, Washington, and Cassiar, British Columbia, batholiths.—The Colville and Cassiar batholiths are discussed together as they both illustrate the results of continued magma move-

ment after much of the complex is solid. The following summary has been made from the descriptions by Waters and Krauskopf (1941) and by Poole (1956).

The Colville batholith intrudes folded and dynamically metamorphosed sedimentary and volcanic rocks of late Paleozoic and Triassic age. The age of the batholith is thought to be late Jurassic or early Cretaceous. It is about 30 miles long. Waters and Krauskopf describe the batholith as remarkably heterogeneous both structurally and petrographically. A central mass of structureless granodiorites grades outward into a belt of foliated igneous rock which commonly shows intricate swirling of the foliation. These swirled rocks grade into a peripheral belt of variable but well-foliated migmatitic gneisses characterized by severe granulation of the constituent minerals. Over broad zones they find that this rock is a mylonite and that locally recrystallization has produced types resembling metamorphic granulites. The trend of the folds (in the country rock) as well as the direction of foliation and other structural features is predominantly northwest-southeast, and across these structural trends the batholithic border cuts with decided discordance. The wall rocks at the periphery of the Colville batholith show almost no evidence of contact metamorphism. Pegmatites are abundant near the border. From detailed consideration of relations both within the wall rock and within the adjacent intrusion, however, Waters and Krauskopf suggest that the features of the contact zone can best be attributed to the rise and emplacement of the batholith as a unit. By this interpretation they infer that the intense brecciation and usual lack of metamorphism in the wall rocks is due to a rise of the intrusive at a time when its peripheral portion (which now forms the gneissic and mylonitic facies) was nearly solid. Where the linear structure shown by swirl axes is well developed, the prevailing pitch of the axes is invariably northwest. They take this to indicate at least a slight regional control of this structure. The core of the intrusive mass is homophanous and composed of granodiorite and quartz diorite.

The following description and interpretation of certain phenomena shown by the Cassiar batholith is taken from Poole (1956). The batholith is of late Jurassic or Early Cretaceous age and is 13 miles wide by 70 miles long. The country rocks are sedimentary and volcanic rocks regionally folded and metamorphosed in the greenschist facies or of lower metamorphic grade. The Cassiar batholith is largely a biotite granodiorite and quartz monzonite. The western part of the batholith for a width of about 4 miles is a strongly foliated cataclastic gneiss, whereas the interior and the eastern part is effectively massive though foliated in places. The central and eastern part is relatively undeformed. There is evidence for shouldering aside and uplift during the emplacement of the magma although it is unlikely that all the space occupied by the batholith was made in this manner. Poole infers that the cause of the deformation of the western border zone was renewal of intrusion in the solid state such that the northeast part of the batholith and adjoining sedimentary rocks moved up and perhaps southwest relative to the southwest border zone, producing the northeast dip of the foliation. He notes that the sedimentary rocks for several miles southwest of the batholith are in isoclinal folds with a southwest dip, and it is unlikely that this would have persisted if regional deformation had acted to produce the northeast-dipping foliation of the west part of the batholith.

Precambrian Batholiths of Mesozone

General statement.—It has been noted that stocks emplaced in the epizone may be of Precambrian age, and so also may Precambrian stocks and batholiths belong to the mesozone. The Giants range (Allison, 1925) and the Vermillion (Grout, 1925) batholiths in Minnesota may be examples, and descriptions of others follow.

Noranda-Senneterre belt, Quebec.—Several batholiths of granite and granodiorite occur as intrusives in a series of intermediate and basic flows with subordinate tuffs of the Keewatin series and Timiskaming sediments in the Noranda-Senneterre belt, Quebec. The country rocks have complex structure and a low-grade regional metamorphism. Norman (1945) and Tremblay (1950) have described some of these batholiths, and a map and description of structure on which Figure 10 is based have been published by Dawson (1954).

The batholithic rocks include muscovite and muscovite-biotite granites and hornblendic varieties; the hornblendic varieties are quartz poor.

The boundary of the La Motte batholith is almost wholly conformable with the foliation of the country rock but does transgress a series of metasedimentary beds at one locality. The foliation indicates an elongate domal roof

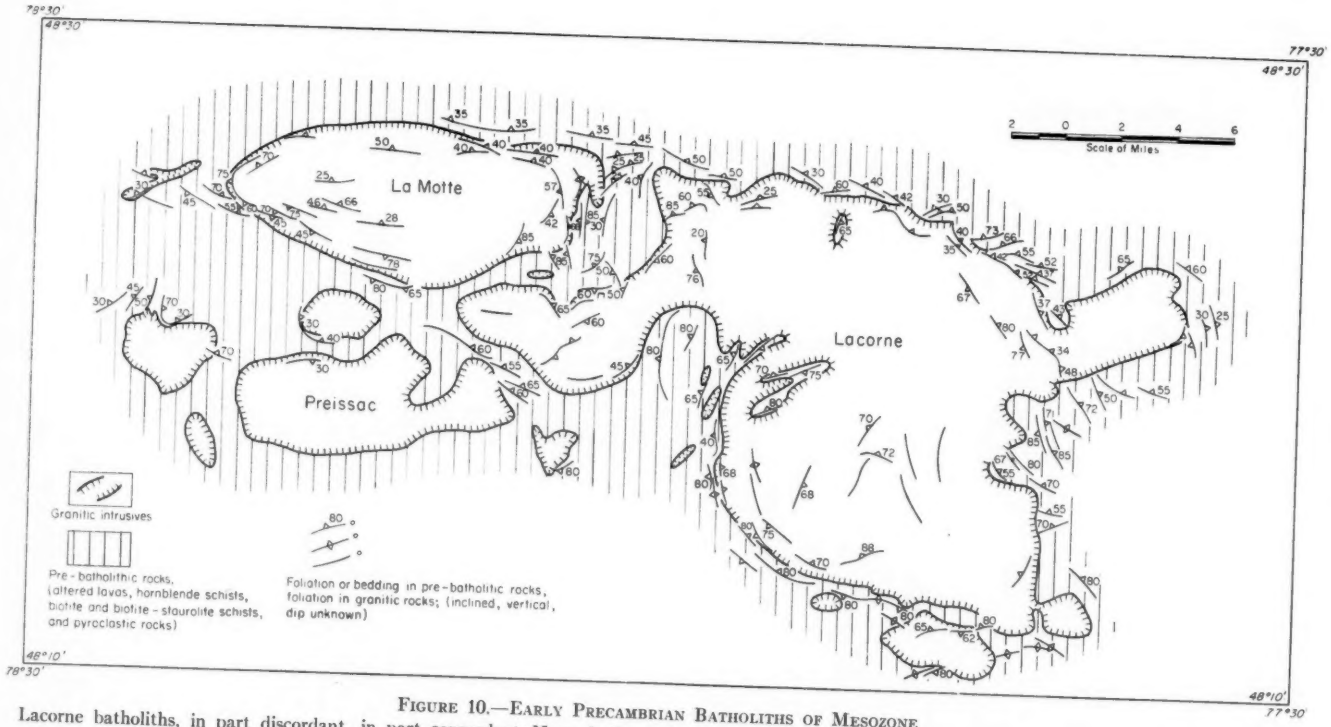


FIGURE 10.—EARLY PRECAMBRIAN BATHOLITHS OF MESOZONE

Lacorne batholiths, in part discordant, in part concordant; Noranda-Senneterre belt, Quebec; Canadian shield. Modified after K. R. Dawson (1954)

with moderately dipping walls on the north and steeply dipping borders around the rest of the pluton. Migmatization occurs very locally. Pegmatite forms nearly 50 per cent of the rock in a zone half a mile to a mile wide around the border of the pluton and at least 10 per cent of the interior of the pluton.

The Lacorne batholith has borders which are essentially concordant on the north and south but which on the east cut directly across the strike of the enclosing formations. Migmatization occurs locally near the southwest border of the pluton. Certain large inclusions have been moved from the vicinity of the walls and rotated. Thin lenses and dikes of granitic material have been injected in peripheral metasedimentary rocks. The foliation of the pluton indicates a structural dome in the northeast part of the main mass and another in the southwest part. As in the La Motte pluton the north border dips moderately, and the south border steeply. Dawson infers that the Lacorne pluton originally had steeply dipping walls and may have been slightly overturned toward the southwest.

The satellitic intrusions are interpreted as unroofed cupolas that join the main granite mass at depth.

Dawson (1958, p. 232) on the basis of a multivariate variance analysis of the mineralogical compositions concluded that the batholiths are composed essentially of a quartz monzonite that is homogeneous within the individual massifs and also within the intrusives as a whole.

The intrusions are all interpreted by the authors as of magmatic origin. The age determination (Shillibeer and Cuming, 1956) of mica from the Lacorne pluton by the K^{40}-A^{50} method gave 2500 ± 150 m.y.

Plutons north of Great Slave Lake, Northwest Territories.—Batholithic emplacement in Precambrian rocks north of Yellowknife on Great Slave Lake, Northwest Territories, Canada, has been described by Henderson (1943) and Jolliffe (1944), and the following is an abstract of their work. The country rocks away from the intrusions (Fig. 11) consist of graywacke, slate, and volcanic rocks. Pillowed lavas are so little metamorphosed that tops of flows can be determined. Chlorite and sericite are common in the graywacke and slate. The rocks are isoclinally folded with steep dips. Henderson believes that the isoclinal folds in turn have been warped into synclinal- and anticlinal-like structures with the axes of the secondary folds plunging nearly vertically. The granitic batholiths of granodiorite and quartz diorite were emplaced in the refolded isoclinal rocks with accompanying metamorphism of the formations in the vicinity into andalusite cordierite and quartz-mica schists (locally with staurolite) and hornfels. The outer boundary of metamorphism crosses the trends of the folds. The granitic batholiths are concordant, and Henderson infers that lateral pressures of invading magma may have produced deformation. The sediments and volcanic rocks dip away from the batholiths at steep angles. There is a series of small younger muscovite-biotite granite stocks that have also produced similar metamorphism of the country rocks. Many granite pegmatite veins are discordant with the foliation of the country rocks.

Supplementary Descriptions of Plutons Emplaced in Mesozone

Introduction.—Other excellent detailed descriptions of mesozonal plutons in the western Cordillera are those by Taubeneck (1957) of the Bald Mountain batholith in Oregon, by Smith (1947) of the Surf Point stock in British Columbia, by Krauskopf (1943) of the Wallowa batholith in Washington, and by Compton (1955) of the Bald Rock batholith in California. Plutons emplaced in the mesozone are also dominant in most other orogens, but descriptions of only the Snowbank stock in Minnesota and the Enchanted Rock batholith in Texas will be referred to here.

Bald Rock batholith, California.—The Bald Rock batholith, California, described in detail by Compton (1955), shows many characteristic phenomena of the mesozonal batholiths. The Bald Rock batholith is one of four plutons in a chain somewhat more than 40 miles long of small satellitic intrusions that lies 20 miles west of the main Sierra Nevada batholith. The batholith is about 9.5 miles wide, a little more than 11 miles long, and has an area of about 80 square miles. The bedding of the country rocks swings concordantly around the batholith, and Compton interprets it as formed by a forceful intrusion. However, he also notes that local crosscutting relations show that about a fourth of its area at the exposed level was gained by other means, and that large concentric outliers and a hull of injection migmatite suggest stoping. Inclusions are scarce, but gradational zoning of the batholith from a trondhjemite core through granodiorite to a heterogeneous tonalite rim suggests that

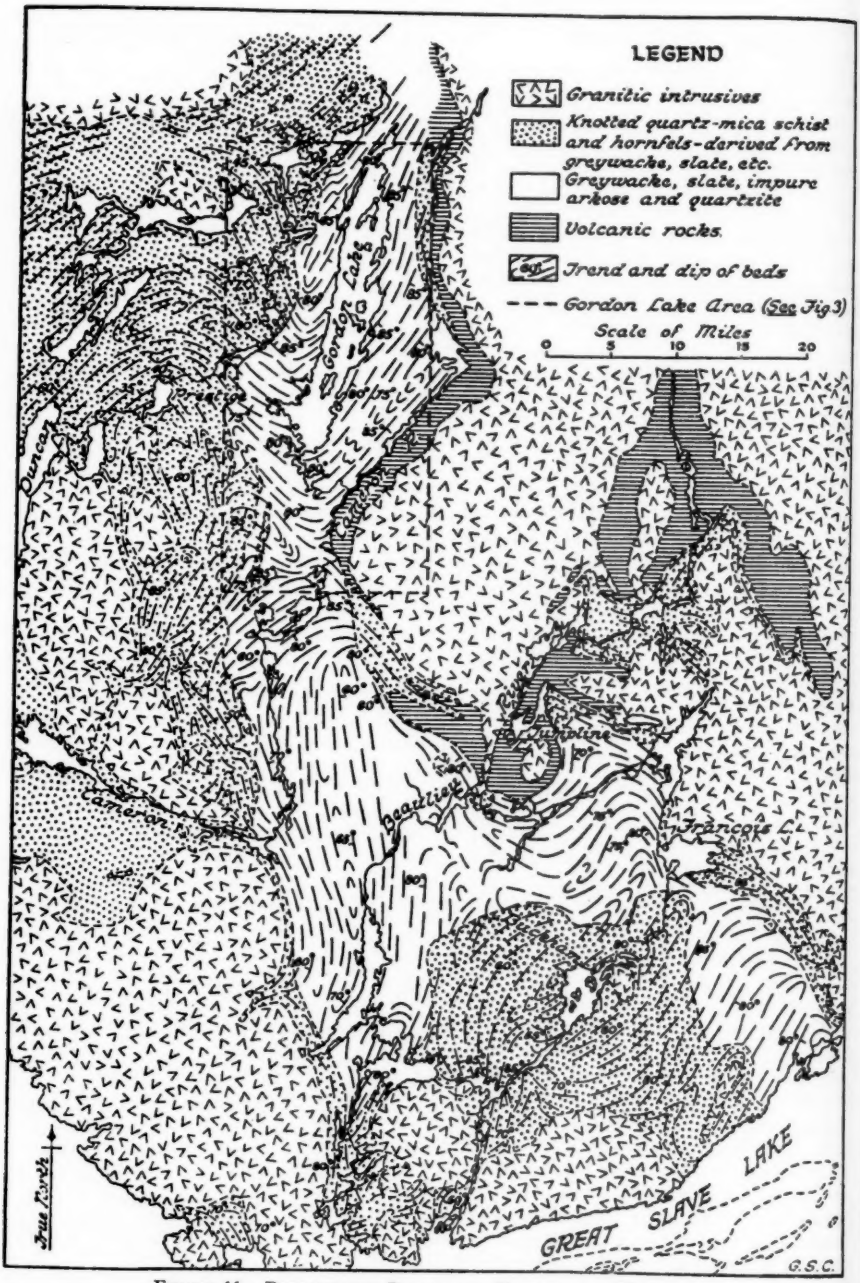


FIGURE 11.—PRECAMBRIAN BATHOLITHS EMPLACED IN MESOZONE

Note discordant boundary of zone of metamorphism; from Henderson (1943) reproduced by courtesy of the American Journal of Science

basic stoped rock contaminated an originally trondhjemitic magma.

Contact-metamorphic rocks of epidote amphibolite to possible pyroxene hornfels form an aureole that has an area nearly as great as the original kinetic intrusion. Squeezing and vertical stretching of wall rocks is indicated by pebbles of conglomerates and crystal lineation, most pronounced near the contact.

The zone of the contact migmatites is only a few feet to a few tens of feet wide where country-rock foliation is parallel to the contact; but it is as much as a quarter of a mile wide where the contact is sharply discordant to foliation. Most of the granitic parts of the contact migmatites occur as sharply bordered dikes that generally parallel foliation but locally cross it. The flow structure of the intrusives is more obvious near the contact because mafic minerals and inclusions are here most abundant, but its actual perfection, grain to grain, does not vary greatly from the rim to the core of the intrusion. In some places the flow surfaces parallel the gradational boundaries between rock types, in other cases they cut across them at large angles. There are several extensive, unconformable junctions of the flow lines that are probably local intrusive contacts. Notably, the flow structures dip as steeply at the core as anywhere in the intrusion. In the west half of the pluton there are thousands of thin aplite and pegmatite dikes, in the east half several large dikes and pipes of aplite and microgranitic rocks. Almost all the dikes are vertical and trend at about right angles to the flow structure. Thus they fan out on the flanks of the trondhjemite mass. The late-emplaced bodies in both halves of the batholith are interpreted as controlled by radial fractures resulting from upward pressure of an underlying mobile core. The way in which the flow layers locally cut across the gradational rock boundaries poses a considerable problem. Compton's suggestion is that immobile tonalite was forming near the contact while granodiorite was forming somewhat farther from the contact, and in some cases while trondhjemite was forming still further from the contact. He believes the flow structures and their overall pattern can be explained only by assuming that the magma was mobile during the growth of the batholith and that grain orientation took place when a zone of mobility slowly grew into the intrusion from its walls. Larsen and Poldervaart (1957) state that

"The distribution of two distinct zircon populations in the Bald Rock batholith as well as structural relations demonstrated by Compton, are explained in terms of a parautochthonous intrusive of migma-magma, with solid phases predominant at the borders of the pluton and silicate melt predominant in the core".

Larsen and Poldervaart emphasize that xenoliths are concentrated between the trondhjemite core and granodiorite-tonalite rim but are rare in the rim itself.

The Merrimac pluton to the north, described by Hietanen (1951), shows many similar phenomena.

Snowbank stock, Minnesota.—The Precambrian Snowbank stock, Minnesota, described by Balk and Grout (1934) is a very fine example of a typical stock emplaced in the mesozone. It is an elliptical mass, 3 miles wide by 5 miles long, with planar foliation in the borders and a faint linear structure throughout, although a late granite portion is almost massive. The country rocks are strongly crowded outward with structures largely conformable with the contact, and the magma rose steeply as a cylindrical mass at an angle of about 70°.

Enchanted Rock batholith, Texas.—A pluton emplaced in quartzo-feldspathic gneisses and high-grade metamorphic schists has been described by Hutchinson (1956) as the Enchanted Rock batholith from the Precambrian of Texas. Although of Precambrian age and intruded in high-grade metamorphic rocks, the batholith has some characters of those emplaced in the mesozone. It is also exceptionally interesting in that one-third of the batholith has a phacolithic relationship to the country rock. The batholith is 9 miles wide and 15 miles long. The batholith shows predominantly a peripheral concordance of the country rock with the border of the pluton, with minor discordance. Except for the phacolithic part of the batholith the foliation is nearly vertical throughout. The lineation is also nearly vertical, and during the early stages of intrusion and crystallization the principal direction of transport is inferred to have been vertical. Marginal fissures are restricted to the outer mile-wide perimeter, dip 10°–25° inward, and are filled with pegmatite and aplite. There is one joint system with steep dip, subradial and at right angles to the planar structure, also filled with pegmatite and aplite. Chilled border rocks are 10 to 2 feet wide. Hiatal porphyritic texture prevails in chilled borders and apophyses. The phacolithic part occupies a synclinal trough plunging 35°–40°. There are four concentric zones of different granitic facies within the pluton.

Hutchinson infers that the batholith was emplaced at a late stage in the deformation by forceful injection and that not more than 5 per cent of the batholith is of replacement origin. The age given by the "Larsen" method is 815 m.y.

Plutons of Transitional Mesozone–Catazone

General Discussion

In a number of regions part of the plutons have characteristics of the mesozone, and part those of the catazone, although both are of similar age. Individual plutons also have some characteristics of both the mesozone and the catazone. Such mixed associations or characteristics appear to occur particularly in plutons emplaced in rocks with an intermediate grade of metamorphism; that of the epidote-amphibolite or staurolite-kyanite subfacies. Where plutons are of similar age in the same region, yet vary from mesozonal to catazonal, it seems probable that we are dealing with local variations in the physical conditions at the site of emplacement rather than with different depth zones. In many such examples the pluton with characteristic of the catazone may be the roof facies of a mesozonal batholith.

Plutons of Wolverine Complex, British Columbia

Armstrong (1949) describes the Wolverine complex as occupying more than 1000 square miles in British Columbia. According to him it includes a series of micaceous quartz-feldspar gneisses (in part with 40 to 65 per cent quartz) and migmatites with granodiorite plutons (up to 10 square miles) formed in place by progressive injection of granitic material and gradual replacement of injected rock. Roots (1954) considers the complex was formed by a metamorphism and granitization superimposed on previously regionally metamorphosed Proterozoic and Lower Cambrian sedimentary beds whose grade of regional metamorphism increases in intensity with successively lower stratigraphic horizons, low-grade quartz-chlorite schists; crystalline limestone, slate, phyllite, chloritoid schist, and graywackes in the upper part of series; quartz-mica schists, quartzite, garnetiferous schists, and kyanite and staurolite schists in the lower part of series. The regional metamorphism he believes preceded folding, and the temperature rise was due in part to emplacement of underlying igneous or anatectic material and to stress produced by relatively gentle orogenic deformation. Granitizing fluids developed leucogranite some of which consolidated in place; some was mobilized and traveled along foliation planes and fractures in partly granitized metasediments to form sills and dikes. A stock of granodiorite (5 square miles) with sharp contacts, steep walls, and a flat domed roof intrudes the schists.

Plutons of Shuswap Complex, British Columbia

According to Cairnes (1940) the area of the Shuswap complex may be more than 4000 square miles and consists of intensely metamorphosed Precambrian beds of Belt (?) age about Shuswap Lake, but in other areas may include Upper Paleozoic and probably Triassic formations. The metamorphic complex contains abundant pegmatites, gneisses with aplitic injection material as an important constituent, great bodies of granitoid gneiss, massive granite with many bodies of pegmatitic granite, and a "sill–sediment" complex of crystalline schists and sill-like bodies of granite gneiss. He believes that the principal processes have seemed to involve a gradual upward seepage of this material (pegmatitic and aplitic differentiates), infiltration along bedding planes, replacement or partial replacement of intervening rock matter, and the growth, *in situ*, of perhaps much of the pegmatitic granite. He suggests that, in places, the continued supply of magmatic material resulted in the complete conversion of large bodies of the original strata into massive granitoid rock, which, under the conditions of transformation, became partly plastic or molten and, where subjected to local stresses, behaved much as a normal intrusive rock behaves in its contact relation with adjoining rock masses. Cairnes believes the granitization was effected in connection with the emplacement of the Mesozoic batholiths. Armstrong and Roots consider the Shuswap complex the equivalent of the Wolverine complex and date the granitization as pre-Pennsylvanian or pre-Mississippian.

Williamsburg Granodiorite Pluton, Massachusetts

The Williamsburg granodiorite pluton in the Williamsburg quadrangle, Massachusetts, described by Willard (1956), appears to be an example of emplacement under conditions transitional between those of the mesozone and catazone. The following abstract is based

on Willard's report. The country rocks consist of garnetiferous quartz-mica schists, quartzite, marble, phyllite, and amphibolite. The phyllites carry metacrysts of staurolite, and the associated rocks contain randomly oriented xenoliths of schist and quartzite.

The metasedimentary beds are part of a homocline on the east limb of an anticlinorium.

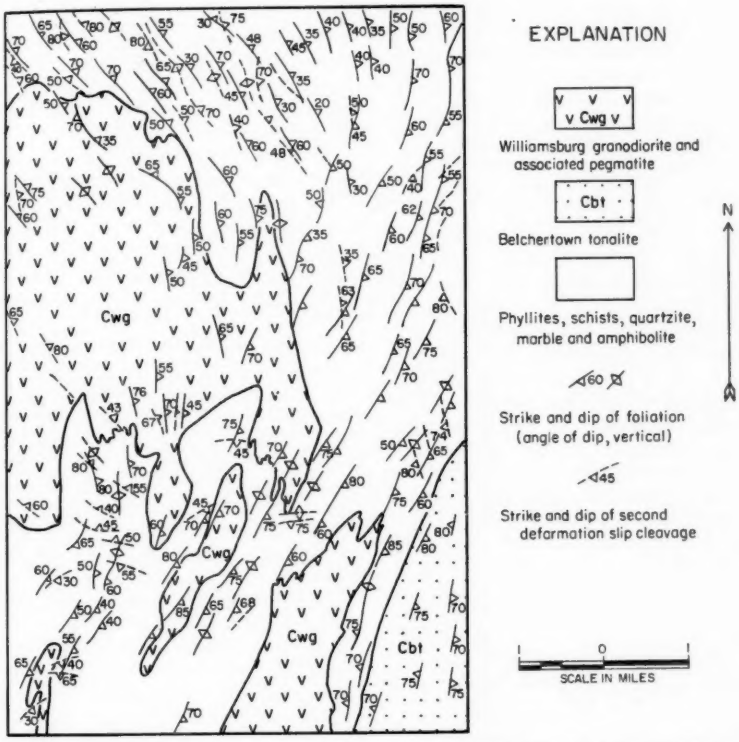


FIGURE 12.—WILLIAMSBURG GRANODIORITE PLUTON OF TRANSITIONAL MESOZONE-CATAZONE Appalachian orogen, Massachusetts. Modified after Willard (1956)

schists locally have metacrysts of staurolite and kyanite, most abundant near the granodiorite. Sillimanite and tourmaline are developed near contacts with the intrusive rocks. The amphibolite consists of hornblende, untwinned calcic plagioclase, with quartz, biotite, titanite, and epidote. The rocks may barely have attained the staurolite-kyanite facies at the time of magma emplacement. The granodiorite is in large part a mixed type consisting of biotite-muscovite granodiorite and of pegmatite, granitic, aplitic, and granodioritic dikes and sills of many sizes. Some of it might be called an injection gneiss. The granodiorite is intruded by granite and pegmatite dikes and sills. At many places the granodiorite and associated rocks contain randomly oriented xenoliths of schist and quartzite.

The schistosity is approximately parallel to bedding on the limbs of folds but cuts across the bedding on the crests and in the troughs. The axial-plane schistosity is inferred by Willard to have been deflected at the north by the force of the intrusion (Fig. 12). Slip cleavage is a planar structure that coincides with the axial planes of small corrugations or microfolds in the schistosity. For the most part the slip cleavage is parallel to the exposed contact between the granodiorite and the country rock. This suggests that the schistosity planes nearest the intrusive moved up relative to those farther away. Willard believes that, in large part, the intrusive forced its way along earlier foliation planes, bending them apart, causing the de-

flections observed in the trend of the schistosity and producing local shear couples that resulted in the slip cleavage that surrounds and dips away from it. The schistosity planes nearest the intrusive moved up relative to those farther away. A northwest-trending slip cleavage was produced by a later deformation. The present writer would also emphasize the discordant relationships between the borders of the intrusive and the country rock, as portrayed both in plan and by the section as drawn by Willard, that relate this pluton to the mesozone.

Lithonia Gneiss (and Stone Mountain Granite of Mesozone), Georgia

The Lithonia gneiss and Stone Mountain granite in Georgia afford another example of a gneiss with characteristics of the catazone inferred to be associated in time and space with a pluton apparently emplaced in the mesozone. The Rb/Sr age of the granite averages 278 m.y. and biotite from the Lithonia gneiss gives 297 m.y. (Pinson *et al.*, 1957, p. 1781).

The Stone Mountain pluton has been described by Herrmann (1954) from whose work the following summary is taken. The country rock is regionally metamorphosed and consists of schists of the staurolite-kyanite or epidote amphibolite subfacies. The muscovite granite pluton in part cuts discordantly across the structure of the country rock and in part crowds the country rock to one side. The flow structure of the granite is in part conformable to discordant contacts with the intruded gneiss. Pegmatite dikes are locally abundant in the schist on the north side of the intrusive, and aplite dikes on the south side.

An independent extensive belt of the schist was injected and replaced by syntectonic, magmatic, potassium-rich solutions which modified it to a gneiss (Lithonia gneiss) of granitic composition. Pegmatite dikes in the Lithonia gneiss are small and irregular; commonly discordant but locally partially concordant aplite forms thin veins. The relationships of the rocks are shown in Figure 13. The migmatitizing and granitizing fluids are thought by Herrmann to be co-ordinate with the magma that formed the Stone Mountain granite. The rocks surrounding the Lithonia gneiss are metamorphosed to the sillimanite-almandine amphibolite subfacies. It is thus a problem to the present writer as to whether the Lithonia gneiss is the roof portion of a mesozonal pluton or represents an earlier emplacement in the catazone

Prospect Porphyritic Granite Gneiss (and Nonewaug Granite Lens of Mesozone), Connecticut

A belt of rocks in Connecticut, regionally metamorphosed in the epidote amphibolite or staurolite-kyanite facies, contains plutons whose characteristics are those of the mesozone. There are also bodies of gneiss formed by migmatization and granitization that seem best classified in the transitional mesozone-catazone.

The Paleozoic Nonewaug granite lens in this belt has been described by Gates (1954). The pluton is 9 miles long and 3 miles wide. The long axis is about N.60°E. and is across the foliation of the schists whose regional trend is north. The schists adjacent to the lens on the north and west borders have in general a foliation parallel to the border of the granite as a result of crowding aside at the time of magma intrusion. On the south border the foliation of the schists is normal to the contact. The southern part of the granite lens, however, is a complex mixture predominantly of granite, pegmatite, and granitic gneisses with subordinate feldspathized schist and schist. The foliation is variable, as in a crumpled zone. The granitic gneisses are granitized schist. The bulk of the granite mass has a layered structure dipping 35°–80° SE. and is inferred to be of magmatic origin. The granite has crosscutting apophyses and also occurs as dikes in the schists. Pegmatite veins are present in the schists. The normal schists are mica quartzites and quartz-mica schists with biotite and muscovite and accessory garnet, staurolite, and kyanite. The characteristics of the pluton seem appropriate to emplacement in the mesozone.

Stewart (1935) has described from a zone southeast of the Nonewaug pluton an extensive belt of porphyritic granitic gneiss formed in schists of similar age and grade of metamorphism by magmatic injection and by permeation and replacement by fluids whose source was in a subjacent magma. Agar (1934, p. 363–369) has also emphasized the extensive occurrence of mixed gneiss resulting from invasion of these schists by granite and pegmatite. These gneisses may be the roof portion of mesozonal batholiths, or they could belong to the upper part of the catazone.

Precambrian Phacoliths of Hanson Lake Area, Saskatchewan

It appears possible that phacolithic emplacement, although characteristic of the catazone,

EXPLANATION
Stone Mountain granite
Porphyroblastic (andesine) biotite gneiss
(includes interlayered amphibolite, biotite schist, biotite gneiss, garnetiferous kyanite schist, kyanite muscovite schist, phlogopite quartzite, muscovite quartzite, and abundant pegmatite dikes)
Amphibolite
(includes epidote–pyroxene–hornblende gneiss, epidote-hornblende gneiss, hornblende gneiss and biotite–hornblende gneiss)
Lithonia gneiss
(even banded biotite gneiss, with local garnet-rich zones; migmatized by syntectonic aplite, pegmatite and granite dikes)
Representative formation boundaries
Foliation
STONE MOUNTAIN
SECTION A—A'
SCALE IN MILES

FIGURE 13.—SMALL PALEOZOIC PLUTON OF MESOZONE (STONE MOUNTAIN GRANITE, GEORGIA)

In part discordant, in part concordant, associated with penecontemporaneous migmatitic gneiss (Lithonia) of transitional mesozone-catazone. Modified after Herrmann (1954)

may also occur in the transitional mesozone-catazone. Byers (1957) has described several syntectonic phacoliths of granodiorite or quartz diorite emplaced in anticlinal structures of biotite gneiss, amphibolite, and migmatitic gneiss of the Hanson Lake area, Saskatchewan. The country rocks are described by him as regionally metamorphosed in the amphibolite facies or the garnet-staurolite zone or staurolite-kyanite subfacies; locally the sillimanite-almandite facies is attained. The anticlinal structures have steeply dipping axial planes and may be asymmetrical or isoclinal.

Syntectonic Pinckneyville Batholith, Alabama

The Pinckneyville quartz diorite batholith, Alabama, has been described by Gault (1945) as a syntectonic batholithic intrusion. It is more than 40 miles long, 8–12 miles wide, and is emplaced in phyllites, schists, quartzites, and amphibolites that have attained only an intermediate metamorphic grade.

Complex History of Great Batholiths, Largely of Mesozone

Introduction

Great batholiths such as those of the Coast Range of Alaska and British Columbia, the Sierra Nevada of California, Southern California, and Idaho have had a most complex history. Individual units have been emplaced, usually in a systematic sequence from more mafic to more alkali-siliceous, to make up composite stocks or small composite batholiths. Such composite plutons have in turn been emplaced as a contemporaneous or successive series within a limited period of time to yield a multiple aggregate that forms part or the bulk of the batholith. Such series may in turn be repeated in periods of time separated by substantial intervals.

The ages of the members of the Sierra Nevada batholith (largely mesozone) have been determined by the Larsen method (Faul, 1954, p. 265) to range in large part between 90 and 111 m.y. and by the potassium-argon method on biotite to be between 82.4 and 95.3 m.y. in general.

The ages of several major members of the Sierra Nevada batholith in the Yosemite National Park area have been determined (Evernden, Curtis, and Lipson, 1957) by the potassium-argon method. The ages for the youngest major member is 82.4 and the oldest 95.3 million years, a range of about 13 million years, and they believe the range is correct to a few per cent at most. The average interval of time between successive intrusions is estimated as 2 million years, and each is inferred to be almost completely crystalline at the time of the succeeding intrusion. The authors propose

> "that room for the batholith was made slowly and in small increments by vertical uplift of the overlying sedimentary rocks which were stripped by erosion as rapidly as they rose. Probably some of the earliest granitic intrusions were at the surface by the time the last intrusion squeezed into place".

The writer would qualify this by suggesting that this mechanism was only one of several factors in emplacement.

The ages of several outlying batholiths within the sedimentary rocks have been determined by Curtis, Evernden, and Lipson (1958) to range between 133 and 143 million years. The intrusives of the two different age groups are believed by the authors to correlate with two separate major orogenic periods—one of Late Jurassic and the other of early Late Cretaceous age.

The Coast Range and Idaho batholiths and the complex of plutons of the northeastern section of the Appalachian orogen all have mesozonal plutons as the dominant elements but also many plutons emplaced in the epizone as younger members.

The ages of a granodiorite and a diorite from the Coast Range batholith of southeastern Alaska have been determined (Matzko, Jaffe, and Waring, 1958, p. 538) to be 93 and 103 m.y. respectively. They note (p. 537) that Silver, Stehli, and Allen have determined a mean age of 103 ± 6 m.y. for four early Late Cretaceous plutonic rocks from Baja California. The Baja California, Sierra Nevada, and Coast Range intrusives would thus seem in part to be of similar age. The Coast Range intrusives, however, are called Late Jurassic to Early Cretaceous in this report.

Coast Range Batholith

The Coast Range intrusives in northern British Columbia are stated by Kerr (1932, p. 305) to comprise nine (more or less) distinct intrusive phases which range in age from early Triassic to late Early Cretaceous. Kerr describes the youngest member, which cuts Lower Cretaceous rocks, as a quartz monzonite poor in mafic minerals, homogeneous, and miarolitic with discordant relations to the country rock.

A coarse grain persists to the sharp contacts except for a narrow chilled edge, in places less than 1 inch. The description suggests to the present writer emplacement in the epizone, and this is in agreement with his own observations of this rock in the Hyder district.

Kerr refers certain dome-shaped bodies of oligoclase granodiorite and hornblende granodiorite to a Jurassic age. The characteristics are consistent with emplacement in the mesozone. He describes as still older a thick sheet of granodiorite which is gneissic throughout and possibly of early Jurassic or Triassic age. Finally there is an older hornblende granodiorite for which he suggests a Triassic age.

The probable emplacement of part of the quartz diorite of the southwest border of the batholith in the catazone has been previously referred to.

Mathews (1958, p. 172–177) has described part of the southern end of the Coast Range batholith that comprises both plutons of Jurassic or Early Cretaceous age and two plutons of post-Late Cretaceous age. The latter are homophanous. Only one of the younger batholiths shows a faint flow structure, and that near the borders only.

There are also small epizonal plutons of slight quantitative volume in the plutonic complex of the Coast Range. One, described by Gault (1945), has developed contemporaneous explosion breccias. A stock of miarolitic granite porphyry is intrusive into Tertiary rhyolitic volcanic rocks of similar composition on Zarembo Island (Buddington, 1929, p. 275).

Idaho Batholith

The complex history of the Idaho batholith has been described by A. L. Anderson (1952). He states that the batholith is composed of discrete masses of granitic rock, some of which came to place under deep-seated conditions, others at much shallower depths. The deeply seated emplacements include two closely related, but separately formed masses; the earlier evolved while deformative stresses associated with a major orogeny were still quite intense, the other evolved during the later less intense stages. Anderson infers that these masses probably had their roots in the same source, but that the granitic bodies introduced under shallower conditions came from a younger probably unrelated source. The oldest rocks of the batholith were emplaced at the close of Sierra Nevadan orogeny hence near the end of Jurassic time. The younger rocks appear to be associated with Laramide structures and are believed to be product of "Laramide orogeny of late Cretaceous time". He describes a "marginal facies", a gneissic quartz diorite along the western side with scattered roof masses in more central areas. The gneissic structure he takes to indicate emplacement during orogeny. An inner facies is largely quartz monzonite without gneissic structure emplaced after orogenic forces had ceased and formed under rather deep-seated conditions as was the quartz diorite. The bulk of the batholith is believed to be of these Sierra Nevadan rocks. The present writer suggests the possibility that the quartz diorite of the western part of the batholith may have been emplaced in the catazone and the quartz monzonite in the mesozone.

Anderson notes that a younger group of rocks, including diorite (of gabbrodiorite type), granodiorite, and quartz monzonite were intruded later and resemble the rocks of the Boulder batholith and its satellites of Late Cretaceous age. The diorite has chilled contacts and hypabyssal characteristics. The granodiorite and quartz monzonite have features he infers to be indicative of fairly rapid cooling and intrusion into the cold older batholithic rocks fairly close to the surface.

Larsen and Schmidt (1958) state that some coarse muscovite-bearing quartz monzonite and some very fine-grained granite of the Idaho batholith have small miarolitic cavities. They also contrast the batholith of Southern California in which the largest unit is about 200 square miles with the Idaho batholith in which several units are more than 2000 square miles each. Their statements for the Idaho batholith, however, are based on reconnaissance only, and detailed work may reveal greater complexity. They interpreted a subordinate porphyroblastic granite facies as the product of granitization of schist. Ages determined by the Larsen method on most of the rocks average 108 m.y., but one pluton gave 57 m.y.

Complex of Plutons in Appalachian Orogen, Northeast Section

A varied series of plutons occur in Paleozoic metasedimentary and metavolcanic rocks in a wide belt of the Appalachian orogen that extends north from Long Island Sound and northeast through Newfoundland. The plutons range in age from late Ordovician (?) or Taconic through Middle to Late Devonian or Acadian to post-Pennsylvanian.

Plutons of Taconic age (about 350 m.y.)

with features characteristic of the catazone occur in Connecticut and New York. These may include the Thomaston granite and granite gneiss (Agar, 1934, p. 363–368) and the Chelmsford granite sheet in Massachusetts (Currier, 1947). Billings (1956, p. 121) tentatively assigns the plutons of the Highlandcroft series a Late Ordovician (?) age. Detailed structural relations of these bodies are not known. They may be of transitional mesozone-catazone type.

Acadian intrusions of Middle or Late Devonian age are abundant throughout the belt. Many have the characters of plutons emplaced in the mesozone. Well-described examples include the La Poile batholith of porphyritic biotite granite in Newfoundland (Cooper, 1954, p. 26–29), the Mt. Waldo batholith of porphyritic biotite granite in Maine (Trefethen, 1944), French Pond biotite granite, New Hampshire (Billings, 1937, p. 508–509, 538; 1945, p. 57–58), binary granite plutons of the Memphremagog area, Vermont (Doll, 1951), the Scituate granite gneiss, Rhode Island (Quinn 1951) of about 306 ± 18 m.y. (Quinn *et al.*, 1957), and the Nonewaug granite lens, Connecticut (Gates, 1954). The Winnipesaukee batholith, New Hampshire (Billings, 1956, p. 128) of age 296 ± 29 m.y. (Lyons *et al.*, 1957), Williamsburg pluton, Massachusetts (Willard, 1956), and Prospect gneiss, Connecticut (Stewart, 1935) have a complex of characteristics and relationships some of which suggest emplacement in the catazone and some the mesozone. They have been tentatively grouped as transitional mesozone-catazone. Billings (1948, p. 122) states that the New Hampshire series of plutons are syntectonic and that the Bethlehem gneiss is injected in giganitic sill-like bodies.

Many epizonal stocks and batholiths occur throughout the length of the same belt and range in age from Late Devonian (?) to post-Pennsylvanian. Examples are the Late Devonian (?) Ackeley and St. Lawrence miarolitic leucogranite batholiths of southern Newfoundland and a granite porphyry batholith of northern Newfoundland. Also, in western Newfoundland Phair (1949, p. 135) reports intrusives of epizonal characteristics that cut Lower Devonian rocks and have furnished pebbles to Mississippian conglomerates. The Mississippian (?) Quincy granite and porphyritic granite stocks of Massachusetts and Rhode Island and the Cowesett granite and granite porphyry stocks of Rhode Island intruded into their related rhyolitic volcanic rocks (Nichols, 1956) are of an age around 270 m.y. (Quinn *et al.*, 1957). Somewhat younger in age—post-Pennsylvanian and about 234 ± 23 m.y. (Quinn *et al.*, 1957)—is the Narragansett Pier granite batholith and the Westerly granites of Rhode Island (Nichols, 1956). The Youngest epizonal plutons are apparently those of the White Mountain series in New Hampshire (Billings, 1956, 129–135) that include the White Mountain batholith, Ossipee stock, and other plutons associated with ring dikes, volcanic rocks, and calderа structure. These plutons give ages of 186 ± 14 m.y., which would suggest Late Permian (?) age (Lyons *et al.*, 1957), though Billings has grouped them as Mississippian (?).

Plutons of the Catazone

"If we relax, we may easily become anarchic—the deeper geology may pass into the higher lunacy" Read, 1951

Introduction

The country rocks in which the plutons of the catazone are intruded are inferred in general to have had a temperature as high as that indicated by the grade of regional metamorphism. This may be a minimum of 450°C. Characteristically this will be at least as high as the amphibolite facies, and the country rocks may consist of amphibolites, metaquartzite, sillimanitic quartz-mica schists, marbles, granulites, orthogneisses, and paragneisses. Associated extensive migmatite zones of semiconformable veined character (phlebites) are diagnostic. There are no chill zones in the plutons. Foliation may be and commonly is well developed throughout the bodies but need not be. It may be steeply dipping throughout parallel to the elongation or periphery of the plutons. Gneissic foliation is common. There is a general conformity between country rock and intrusive. The country rock may be pulled apart as a result of extensive plastic crystalline flow during deformation preceding emplacement of the pluton and also during the emplacement.

Augen gneisses and porphyroblastic granites and granitic gneisses of replacement origin are common.

A migmatitic-like facies may develop locally as a product of metamorphic differentiation.

It has been well established that many plutons or major parts of plutons in the catazone have been emplaced by recrystallization and replacement. It has been equally well es-

tablished that many plutons of the catazone were emplaced predominantly by intrusion of magma. The number of plutons in the catazone, however, for which the mechanics of emplacement is at present indeterminate, problematical, or the subject of controversy probably exceeds by far the total number in the first two categories.

Batholithic bodies, in part, emplaced in the catazone have been referred to in the preceding discussion of the Coast Range batholith of Late Jurassic-Early Cretaceous age, and some Paleozoic plutons of the Appalachian orogen may belong to the catazone, but the most extensive development of bodies emplaced in the catazone is found in rocks of Precambrian age.

Batholiths of the catazone as a whole and in detail may in part crosscut the structural trends of the more rigid members. Characteristic forms for the plutons are domes, phacoliths, and conformable sheets. They are generally interpreted as syntectonic. Many of the masses, however, have irregular forms or are so large and complex as to be indeterminate without further study. Funnel and nearly vertical subcylindrical forms have also been proposed for some plutons.

Domes

Introduction.—Domical plutons are a major form of granite emplacement in the catazone. Several interpretations have been offered for their origin: (1) magmatic emplacement and therefore predominantly igneous, (2) magmatic emplacement with concordant interlayers of country rock (stromatolithic or interlayered xenolithic domes), (3) replacement domes, and (4) tectonic domes by plastic crystalline flowage or (4a) by rejuvenation and remobilization accompanying the introduction of material by fluids. Many igneous and interlayered xenolithic domes may in part have had a phacolithic mechanism of emplacement.

Igneous domes of magma emplacement.—Several igneous domes of magma emplacement are described in some detail.

SALMON LAKE BATHOLITH: The Salmon Lake batholith (Fig. 15, just southeast of Lat. 44°00′ and Long. 74°45′) in the Adirondack Mountains area of New York can be interpreted as a transitional form between a large elongate phacolith and a more nearly equidimensional dome of magma emplacement. The rock of the structure is a gneissoid hornblende granite with mesoperthite the predominant feldspar. The dips at the core of the structure are gentle, but they are steep on the limbs toward the adjoining synclines. The anticlinal structure is brought out by skeletal remnants of members of the Grenville series with its sheets of metadiorite and metagabbro. It may be noted that the lineation of practically all the granite with gneissoid (as distinct from gneissic flow) structure including the anticlinal ovoidal batholiths is subparallel to the strike of the foliation consistent with the late syntectonic emplacement and contrasting with the normal steep lineation of mesozonal batholiths.

KILLINGWORTH, BRANFORD-STONY CREEK, and CLINTON DOMES, CONNECTICUT: A cluster of granite domes described by Mikami and Digman (1957) were emplaced at depths of at least 5 miles. Two of the domes are largely of a microcline-rich granite and have a peripheral zone of migmatite, a third one is tonalite with an interlayered xenolithic facies that forms an outer facies and constitutes a mantling xenolithic dome.

The Killingworth dome consists of tonalite of magmatic origin that grades outward from a eugranitic core into a periphery interlayered with slablike amphibolite inclusions from the country rock. Amphibolite inclusions appear only in minor amount in the central area where they have a random orientation and the foliation of the tonalite flows around them. The tonalite of the peripheral interlayered xenolithic portion is granoblastic and is a slightly earlier facies deformed by continued flow of the interior. The foliation of the dome has gentle dips at the core and moderate to steep dips on the flanks except at the south where the country rock is overturned outward.

The immediate bordering country rock consists of hornblende and biotite gneisses with two-thirds of the gneisses containing more than 35 per cent hornblende. The gneisses are overlain by biotite-muscovite schists.

The Branford-Stony Creek dome has two units, a quartz monzonite as a local border facies and a younger microcline-rich granite as the main mass. The composite body is about 2 miles from the Killingworth dome and is younger. The domical foliation is inferred by Mikami and Digman to have been imposed before complete consolidation on material emplaced as magma. The dips of foliation in the Stony Creek dome are moderately steep throughout. In a few places the foliation of the country rock strikes into the granite at small angles. A few unoriented angular inclusions occur in breccialike habit in the central part of the granite. The metamorphic forma-

tions around the mass in a zone half a mile to a mile wide contain migmatite. The migmatite is interpreted as formed predominantly by forcible granitic injection with some accompanying metasomatism. There is a local development of granite augen gneiss emplaced partly by dilation and partly by replacement. The Clinton dome is similar to the Branford-Stony Brook dome.

IGNEOUS DOMES OF SOUTHERN RHODESIA: The Precambrian domes of Southern Rhodesia have been described by Macgregor (1951). He quotes (p. xxxix) with approval the following statement of Maufe,

> "It is a general rule throughout the Territory that the strike of the schists and their foliation is parallel to the edge of the batholiths and to the banding of the gneissic granite. Secondly, the batholiths, being roughly oval bodies, have curving margins, there being no general direction of strike throughout the country independent of granite batholiths. Thirdly, the schists almost always dip away from the margins of the batholiths, thus appearing to be synclinal areas."

Macgregor suggests that the large ovoidal batholiths probably originated as homogeneous magmas which ultimately consolidated as granite gneiss.

Interlayered xenolithic domes.—The term "stromatolith" was proposed by Foye (1916, p. 791) for "a rock mass consisting of many alternating layers of igneous and sedimentary rocks in sill relationship". The types to which it was applied were granite plutons of the Haliburton-Bancroft area, Ontario (Fig. 14).

HALIBURTON-BANCROFT AREA, ONTARIO: These plutons have a minimum of 20 per cent of layers of gray gneiss and amphibolite. It was inferred that the granite magma was intruded concordantly along foliation planes of the country rock with a doming produced near the center of the intrusion with outward quaquaversal dips. Osborne (1936, p. 426–427) believes that only the border zones of the batholith described by Foye contain so many inclusions.

BLACK HILLS DOME, SOUTH DAKOTA: The following description of the Black Hills Precambrian granite domes is summarized from a report by Runner (1943). The granites of the Harney Peak area are a composite of many sills, tongues, dikes, and irregular masses of various compositions and ages. Within the area are many xenoliths of sedimentary rocks which in the central part are composed of metalimestone and amphibolite. The bedding planes and the axial planes of the isoclinal folds in the sedimentary inclusions in the interior dip outward from the central axial region and form a well-defined xenolith dome. The growth of the dome is believed by Runner to have been from the center outward by marginal intrusion on the border of a laccolithlike structure. As the structure increased in size, marginal dips steepened.

The formation of the Harney Peak dome was preceded in the area by overthrust faulting and recumbent folding. Space for the granite according to Runner was made by domal uplift, lateral spread, and replacement. He suggests that the domes of the southern Black Hills probably coalesce below the schistose sedimentary cover into a major Precambrian batholith. The foliation, he infers, has been produced by flow in the liquid state, replacement of bedding, multiple intrusion, and shearing of solid granite. Many inclusions were isolated by coalescence of parallel sills and by intersecting dikes and sills and were never engulfed in liquid magma. The age of some granite pegmatites in the Black Hills has been determined to be about 1600 m.y.

Tectonic domes and folds of plastic crystalline flowage.—Quirke and Lacey (1941) have concluded that many complex batholithiclike domes with invasive relationships shown by their diverse facies may arise from "mutual plastic invasion of the rock layers by solid flow" under conditions of deep-zone deformation, but this interpretation has not received much application.

NORTHWEST ADIRONDACK AREA: Several bodies of orthogneiss (Fig. 15) with a composition ranging from syenite to granite have been described from the northwest Adirondacks by Buddington (1948, p. 24–30). The rock of all these bodies has a granoblastic texture and evidences of complete recrystallization under conditions of high-grade metamorphism. They are inferred to have structures formed by plastic doming and anticlinal deformation (isoclinal folding at extreme) of original sheetlike or gently phacolithiclike differentiated layers of igneous rock. There is no evidence of any granitization or migmatization in connection with the remobilization and development of these domes and anticlines as in the case of the reactivated domes described by Eskola, although pressure of rising magma beneath the anticlines and domes may have been a factor. The domes are not rheomorphic in the sense that their reactivation has resulted in intrusive relationships to country rock.

Tectonic domes of remobilization with intro-

duction of fluids.—Eskola (1949) set forth a concept of the development of domes in a second period of orogeny which has received wide acceptance. The hypothesis envisages a plutonic mass of an early orogeny later eroded and mantled with sediments. During a later orogenic cycle fluids or new granitic magma was injected into the older pluton at the same time that it was deformed into gneiss with accompanying migmatization and granitization or palingenesis. The old pluton was thus mobilized anew, and associated younger intrusive magma may display an intrusive relation to the mantle rocks.

Eskola (1949, p. 470) suggests that the domes in Maryland described by Broedel (1937) are of such an origin. Precambrian granite gneiss was reactivated in Taconic (?) time by intrusion of granite and granitization. He also suggests that these mantled domes occur in orogenic zones and have apparently been formed under the influence of horizontal thrust movements, although the doming itself is inferred to be due to vertical movements of granitic masses, most if not all of which were caused by swelling during granitization and soaking with granitic magma.

In a later paper Eskola (1952, p. 126) emphasizes that in some domes the element of later granitization is absent or only incipient.

Further discussions of the problems involved in such domes may be found in the papers by Kranck (1954) and by Balk (1946).

Phacoliths

Introduction.—The term phacolith was introduced by Harker (1909, p. 77–78) for concordant intrusive bodies introduced concurrently with folding. He states that the situation, habit, magnitude, and form of the phacolith are all determined by the circumstances of the folding itself and that the ideal type of phacolith is subject to many modifications, in accordance with the varying mechanical conditions of intrusion. Harker also suggests that originally concordant relations may be obscured, owing to the igneous rocks becoming involved in later folding. The original phacolith described by Harker is a dolerite intrusion in a relatively gentle anticline. Most intrusions to which the term has been applied since, however, are syntectonic granitic types in highly deformed rocks and may themselves have been subjected to strong post-consolidation deformation. The phacoliths are characteristically much thickened on the anticlinal plunging noses or in the plunging ends of synclines. They commonly range in size between a mile and a score of miles in length and may be up to several thousand feet in thickness.

Phacolithic intrusions emplaced in the catazone are common throughout the world and have been especially described from the Precambrian shield areas. Excellent descriptions of granite phacoliths in Africa have been published by Gevers and Frommurze (1929) and by Poldervaart and Backström (1949). Several North American examples, all of Precambrian age, are reviewed here to illustrate this mechanism of emplacement.

Phacoliths of Grenville subprovince, Canadian shield.—Phacoliths are abundant in the high-grade metamorphic Precambrian rocks of the Grenville subprovince of the Canadian shield where they have been referred to by Wilson (1925, p. 397). Osborne (1936, p. 426), and Hewitt (1953, p. 92–93), and have been described throughout the Adirondack outlier by Buddington (1929b; 1948; 1956, p. 115–117), Reed (1934); Cannon (1937), and Dietrich (1954). Some of the Adirondack phacoliths occur in marble, and all have a homogeneous and narrow range of composition (Buddington, 1957, p. 295). These relationships along with others make it highly improbable that they were emplaced by replacement but rather as magma. Nearly all those in the marble, 15 in all, have come into anticlines, most of them into anticlines parallel to the major trends, but some into anticlines or synclines that are cross-folds. Extensive phacoliths of replacement origin, however, in many places accompany those of magmatic intrusion.

Phacoliths of the New York-New Jersey highlands.—Phacoliths are also abundant in the highlands belt of Precambrian metamorphic rocks in New York and New Jersey. A synclinal phacolith has been described by Lowe (1950). The granite occurs as a synclinal sheet with a greatly thickened trough and one well-developed limb. Lowe infers that absence of secondary foliation and lack of tectonic fabric patterns in the granite indicates post-tectonic emplacement. He proposes the concept of "exchange of space" between the magma rising and the country rocks subsiding into the emptying magmatic chamber to account for the lack of evidence indicating lifting of the overlying rocks by forcible injection of the granite. The present writer has studied similar granitic plutons some miles to the southwest, and for these there is adequate deformation and recrystallization in much of the rock to justify

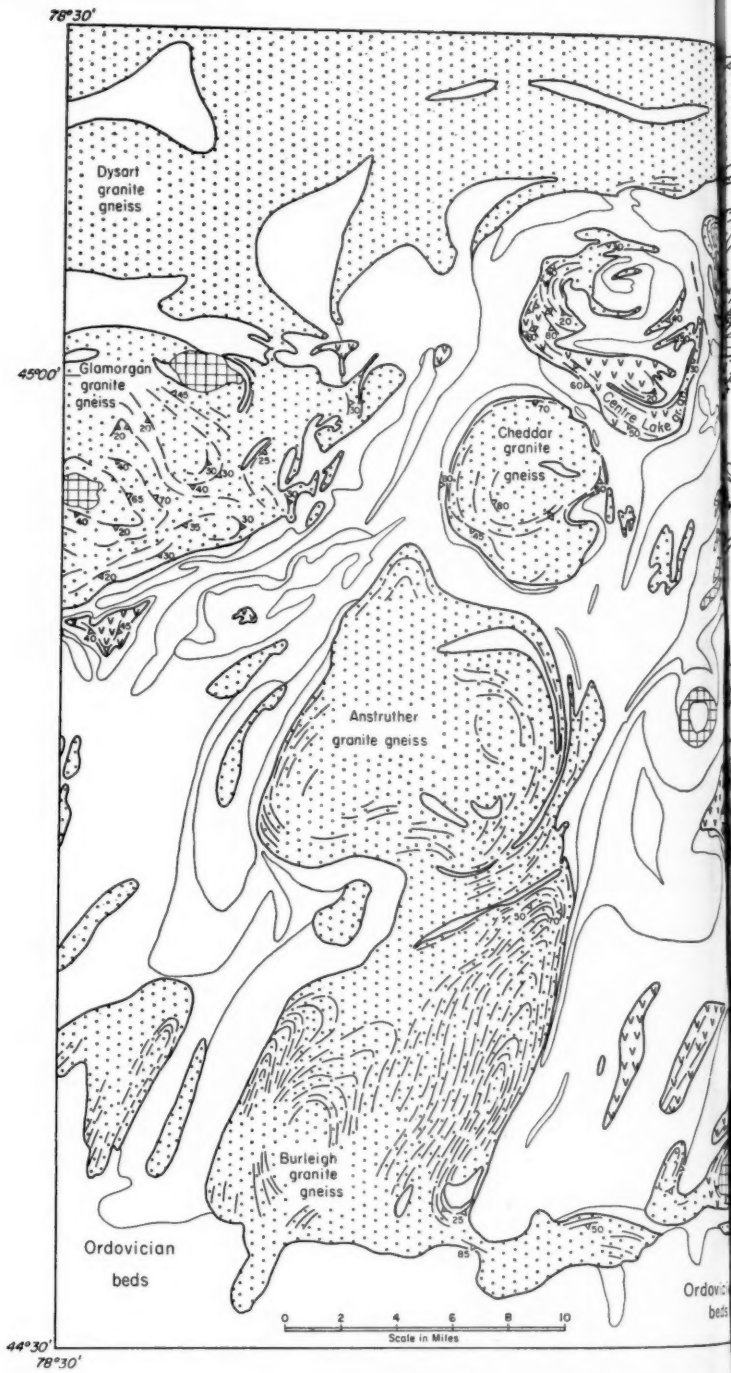
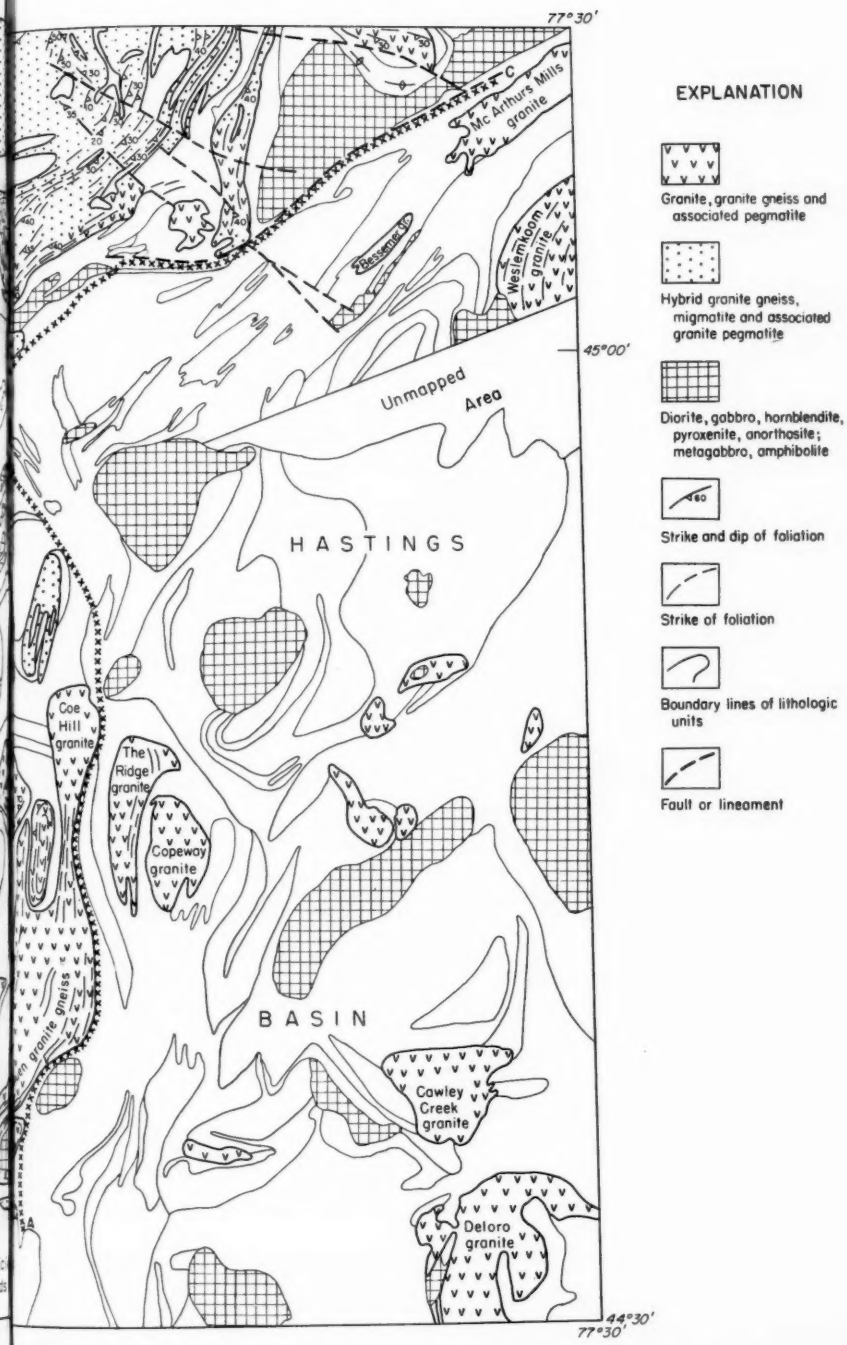


FIGURE 14. GEOLOGY OF PART OF HALIBU

Metasedimentary and metavolcanic rocks of Hastings Basin southeast of line of crosses are of lo
and crystalline marble, and volcanic rocks in greenschist facies. Metasedimentary and metavolcanic r
part sillimanitic, paramphibolite, marble and silicated marble, metagabbro and metadiorite gneis
the granitic gneisses, in large part with domal structure, of the high-grade metamorphic area were em



...croft Area, Canadian Shield

...mediate-grade metamorphism and include conglomerate, argillite, and pelitic schists, blue-limestone ...west of line of crosses are in high-grade metamorphic facies and include migmatites, paragneisses in ...bolite schist from basic volcanic rocks. The granites of Hastings Basin were emplaced in the mesozone; ...catazone. Modified from map 1957-b, Ontario Department of Mines.

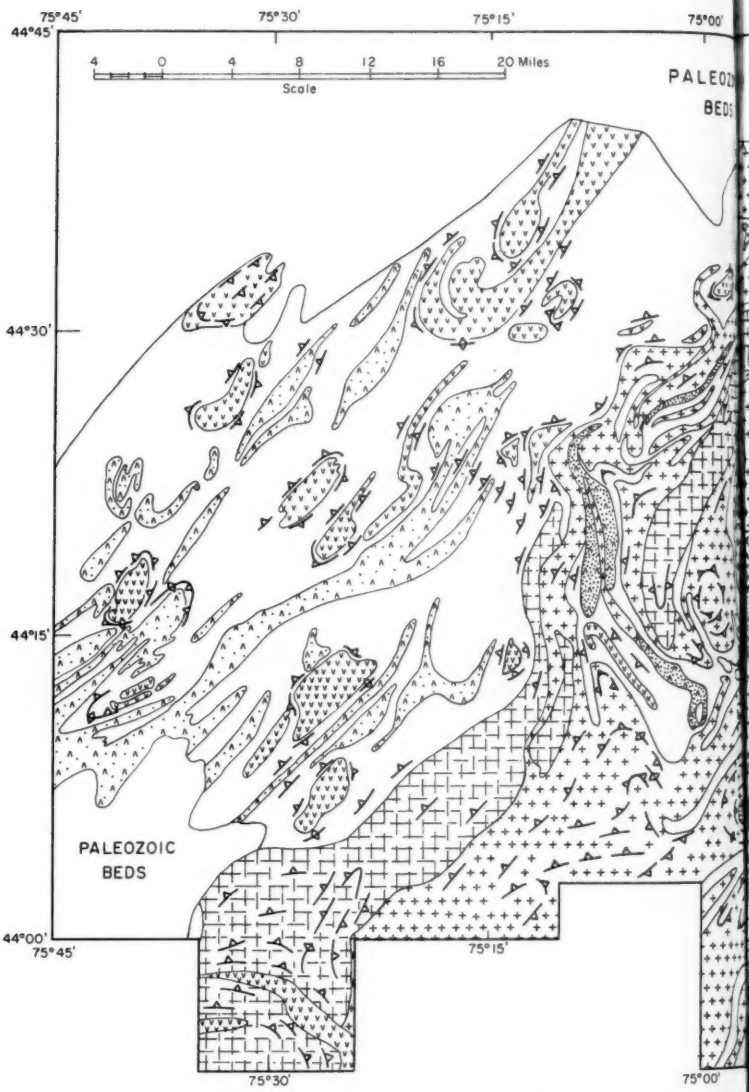
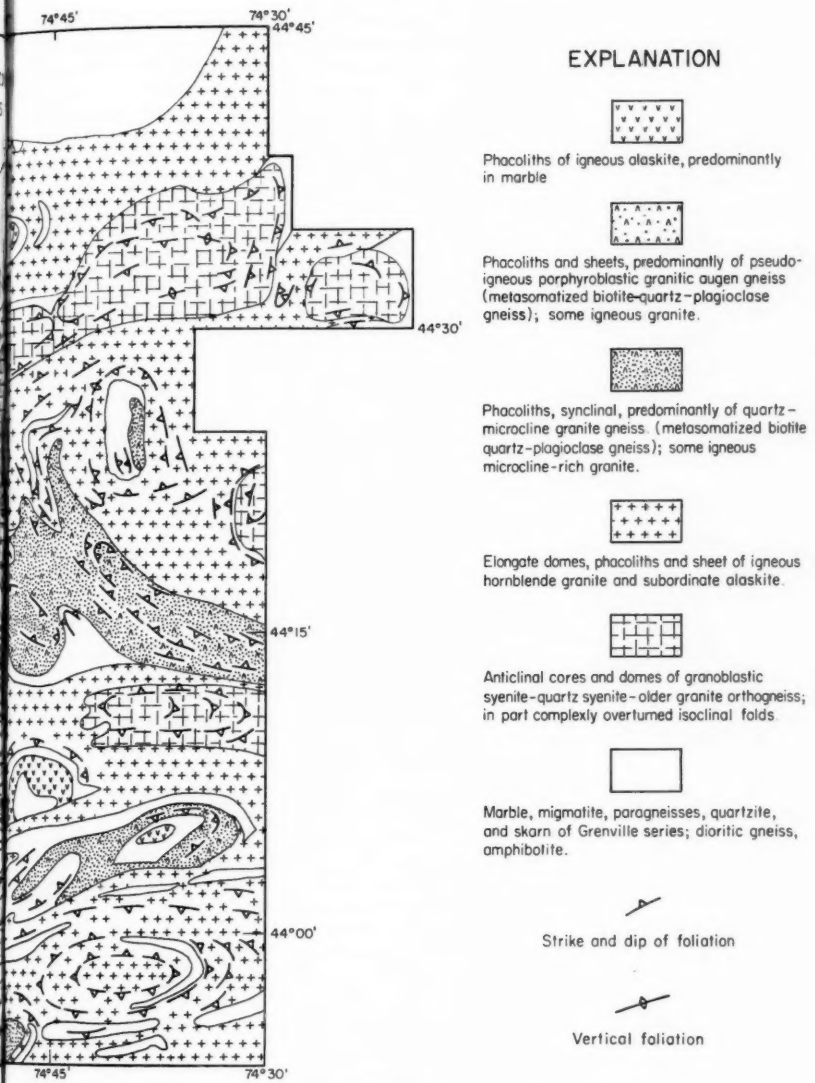


FIGURE 15.—PRECAMBRIAN PLUTONS OF CATAZONE, NOR
Phacoliths of igneous origin, pseudo-phacoliths of metasomatic origin, confor

considering them as late tectonic emplacements and as phacoliths.

A phacolith of pyroxene and hornblende syenite gneiss has been described from the New Jersey highlands by Buddington (1956, Fig. 6). It occurs on a steep anticlinal fold, is more than 12 miles long on one limb with a thickness of 700–800 feet and a thickness of 10 times this amount on the plunging nose of the anticline. Younger granite also occurs as a younger phacolith flanking the syenite gneiss (Buddington, 1956, Fig. 6) on the same anticline. In the area to the northwest of this composite phacolith Hague *et al.* (1956, p. 459) describe phacolithic Byram granite gneiss. They suggest that the lack of large-scale discordant features between


74°45'
74°30'
44°45'
44°30'
44°15'
44°00'
74°45'
74°30'
EXPLANATION
Phacoliths of igneous alaskite, predominantly in marble
Phacoliths and sheets, predominantly of pseudo-igneous porphyroblastic granitic augen gneiss (metasomatized biotite-quartz-plagioclase gneiss); some igneous granite.
Phacoliths, synclinal, predominantly of quartz-microcline granite gneiss (metasomatized biotite quartz-plagioclase gneiss); some igneous microcline-rich granite.
Elongate domes, phacoliths and sheet of igneous hornblende granite and subordinate alaskite.
Anticlinal cores and domes of granoblastic syenite-quartz syenite-older granite orthogneiss; in part complexly overturned isoclinal folds.
Marble, migmatite, paragneisses, quartzite, and skarn of Grenville series; dioritic gneiss, amphibolite.
Strike and dip of foliation
Vertical foliation

NDACK AREA, N. Y., OUTLIER OF CANADIAN SHIELD
igneous domes, and tectonoplastic domes and anticlinal cores of orthogneiss

the Byram gneiss and other rocks indicates that the Byram was formed either as a phacolithic intrusion or by replacement of a large metasedimentary sequence and that most of the field and microscopic evidence points to an igneous origin. They conclude that the Byram gneiss may have had a complex history of igneous intrusion coupled with partial replacement.

Phacolithic emplacement of plutons in the New Jersey highlands has also been described by Hotz (1953, p. 185–192) and by Sims (1953, p. 265–268).

Wolf Mountain phacolith, Texas.—The Precambrian Wolf Mountain phacolith has been

described by Stenzel (1936). He suggests that the granite intruded as a phacolith into the trough of a syncline that pitches on an average 16° SE. The granite is underlain by gneisses and overlain chiefly by schists. The intrusion he believes took place toward the end of the period of folding of the country rock and was accompanied by the stress that produced the folds. Stenzel infers that the feeding channels of the intrusive body are in a long shear zone, which extends along the phacolith and cuts across the schistosity of the country rock. Thus the magma, after rising in this moving shear zone, spread out into the syncline along the boundary between gneiss and schist.

Harpoliths.—The angle of pitch of the axes of phacoliths may range from gentle to 90°. The name "harpolith" was originally introduced by Cloos (1921, p. 44–47, 84–85) for intrusions of sickle-shaped form emplaced contemporaneously with the formation of cross folds in steeply folded rocks. There are numerous harpoliths in the Precambrian of the Adirondack area. The synclinal phacolith described by Dietrich (1954) could be called a harpolith.

Replacement pseudo-phacoliths.—Some phacolithiclike granitic masses are in large part the product of granitization and metasomatism, such as the Hermon pseudo-phacolith of the northwest Adirondack area, New York, and the sheet of granodioritic gneiss of the Manawan Lake area, Saskatchewan, described in sections that follow.

Ambrose and Burns (1956, p. 49–52) have inferred that the granite sheet conformably surrounding the Clare River syncline of the Grenville series in Ontario is of replacement origin, primarily because of the general conformity of long thin septae of limestone and the lack of disturbance which they infer should accompany magmatic emplacement. The present writer, however, is convinced of the possibility of essentially conformable syntectonic emplacement of magma in folded rocks.

Quirke (1929) has described a series of Precambrian intrusives from the French River area, Ontario, which he calls batholiths. His description of the structural relationships, tectonic history, and his interpretation of their origin, however, permit them to be called replacement phacoliths. The country rocks are metasedimentary rocks and migmatites. The plutons consist primarily of granitic and syenitic rocks. The major structures of these areas according to Quirke are connected by a unifying but peculiar major fold. It is fan-shaped with its apex to the north, to which converge anticlines, synclines, and fault lines. The batholiths conform to the country gneisses of this structure. The masses of plutonic rock are in general small, less than 15 miles long and less than 5 miles wide. Quirke states that the intrusive lenses are inclined to widen along the axial region of the great syncline, indicating that intrusion and folding were closely connected in origin. The granitic rocks appear to him to be replacements of sedimentary rocks, and he cites as one line of evidence that the phenocrysts in some certainly have grown within gneisses which still are easily distinguishable as sedimentary rocks, and that these gneisses grade into masses which are so exclusively porphyritic that no trace of other structure or texture remains visible.

Phacolithic and pseudo-phacolithic emplacement, Manawan Lake area, Saskatchewan.—Complex phacolithic emplacement appears to be well exemplified in the Manawan Lake area, Saskatchewan. The area has been mapped and described by Kirkland (1956), and a part of the geologic map is shown in Figure 16. The plutons were not designated as phacoliths by Kirkland, but the structural data given are consistent with such an interpretation. The rock mapped as granodiorite gneiss is described as a strongly foliated or finely gneissic rock composed of quartz and feldspar with hornblende the most abundant mafic mineral. In many places minor amounts of nodular meta-arkose, biotite gneiss, cordierite-biotite gneiss, and hornblende gneiss also occur. The granodiorite gneiss occupies the same position on the east side of the Lake Manawan dome (L.M.) as the meta-arkose does on the west side, and the granodiorite gneiss is inferred by Kirkland to be a more highly metamorphosed granitized equivalent of the meta-arkose.

The conformable phacolithiclike core of the Lake Manawan dome consists of leucocratic porphyritic to even-grained granodiorite. The plagioclase exhibits albite and Carlsbad-albite twins. The rock is generally massive but in places weakly foliated. The granodiorite is interpreted by Kirkland as intrusive.

Subcylindrical Plutons

Wynne-Edwards (1957) has described the Westport pluton in Ontario as that of an almost vertically plunging cylinder emplaced in a vertical cylindrical fold or "vortex" that formed a natural vertical channel for the uprise of magmas and/or granitic emanations. The

cylindrical fold resulted from a deformation of previously isoclinally folded metamorphic rocks of the Grenville series that caused rotation about a vertical axis expressed by buckling of competent bands along the strike and in certain places of flowage of incompetent layers into "vortices". The pluton is formed in part by gabbro but in large part by monzonite that replaces gabbro, paragneiss, and marble. The pluton is about 15 square miles in area, and the foliation of the country rock is conformable with the margin of the mass. Numerous relics of country rock occur within the pluton, and their foliation conforms to the attitude of the external mantle. There are several such plutons in a row close together. The plutons are inferred by Wynne-Edwards to be post-orogenic, emplaced in a dilatant zone with no indication of flow structure. A syntectonic mechanism of emplacement is considered improbable because of lack of flow structure or of post-emplacement deformation.

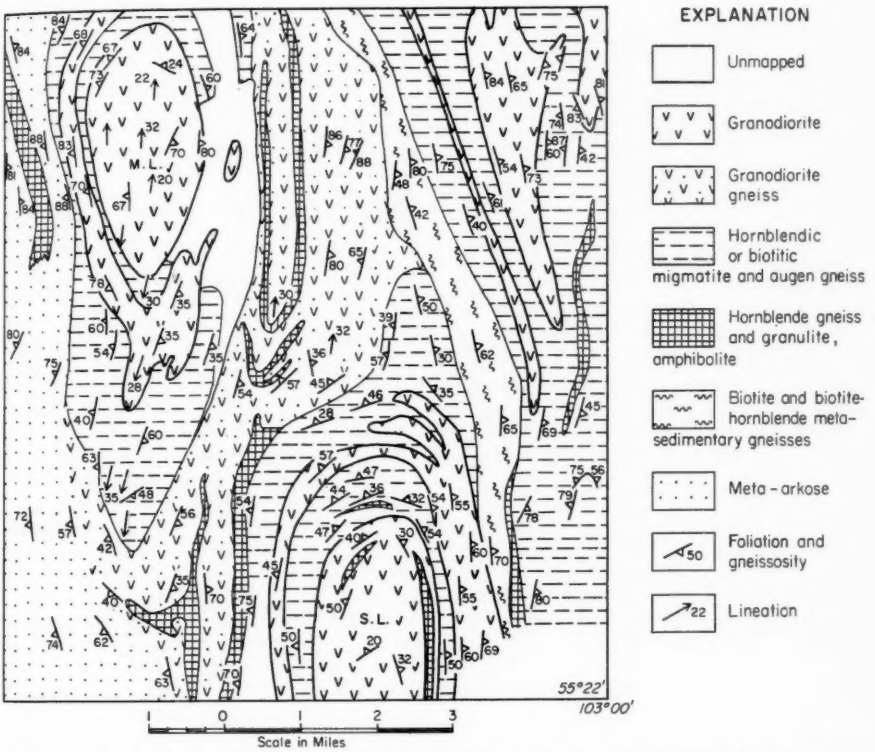


FIGURE 16.—COMPOUND GRANODIORITE PHACOLITHS (M.L. AND S.L.) OF INTRUSIVE ORIGIN AND PSEUDO-PHACOLITH OF GRANODIORITIC GNEISS (RECRYSTALLIZED AND GRANITIZED META-ARKOSE IN PLACE), CATAZONE

Modified after part of Manawan Lake area, Saskatchewan, by S. J. T. Kirkland (1956)

Emplacement in the Grenville Subprovince, Canadian Shield

General statement.—The Grenville subprovince of the Canadian shield includes a belt more than 250 miles wide and more than 1000 miles long consisting preponderantly of uniformly high-grade metamorphic rocks and igneous plutons of the catazone. The province includes the Precambrian outlier of the Adirondack area in New York. The rocks of the highlands of New Jersey are similar. Many aspects of the area are discussed in *The Grenville problem* (Thomson, 1956). Age determinations (Shilliber and Cumming, 1956; Eckelmann and Kulp, 1957) lead to the inference that the

granitic intrusions in the Grenville series of the general Haliburton-Bancroft area, Ontario, are 800–900 m.y. and 1050 ± 20 m.y. old.

Plutons in the Grenville series of Quebec.—Osborne (1947) has had much experience with the geology of the Quebec part of the Grenville subprovince, and the following statements are based on some of his conclusions. The type locality for the Grenville series lies within a dejective zone. Within this zone the intrusives tend to be concordant with the Grenville rocks. Between the dejective zones are broad areas characterized by schistosity parallel to bedding and by gentle dips. In addition to sills in these areas there are batholiths of coarse-grained granite that cut across the structure. Osborne notes that some measure of syntexis is observable, particularly in the dejective zones, and that members of the normal sedimentary series may be missing, in which case a variety of granitic rock occurs in its place. He suggests that magma appears to have been the dominant constituent of the syntectic but that at a few localities the granitic gneisses were formed by granitization of paragneiss. In the Ottawa folded belt Osborne (1936, p. 426) finds that most of the intrusives as a whole partake of the nature of phacoliths.

Plutons of northwest Adirondack area, New York.—Several types of emplacement of plutons in the catazone are well represented in the Grenville series of the northwest Adirondack area, New York, and outlier of the Canadian shield. Representative structural relationships are shown in Figure 15.

In the northwest part of the area is a belt about 25 miles wide in which members of the Grenville series are predominant. The granitic plutons occur as alaskite phacoliths of intrusive magmatic origin, mostly in marble, and as sheets of porphyroblastic augen gneiss formed largely by metasomatism of biotite-quartz-plagioclase gneiss interbedded with marble. Most of the phacoliths have moderate plunging axes parallel to the major trend of the formations, but a few are in crests or troughs of cross-folds plunging nearly at right angles to the trend of the formations. The phacolith at the extreme northwest is emplaced in a cross-fold plunging southeast in beds isoclinally overturned to the northwest with steep dips. Several small phacoliths along the northeastern half of the southeast border of the Grenville belt are also on cross-folds, here plunging northwest. The phacoliths along the northwest and southeast portions of the Grenville belt are in zones of isoclinal overturning to the northwest and southeast respectively and are granoblastic gneisses. In the central part of the belt, however, there are phacoliths with gneissoid mesoperthite granite.

The largest body of pseudo-igneous porphyroblastic augen gneiss in the Grenville belt is the Hermon pseudo-phacolith (Fig. 15, Lat. 44°25′ Long. 75°15′ to Lat. 44°08′ Long. 75°45′). The rock is predominantly a gneiss with augen of microcline in an even-grained gneissic groundmass. The phacolith has a minimum length of 35 miles and a width of 1–3 miles. The granitic mass is continuous at the southwest around the plunging nose of a subordinate anticline and the trough of a syncline. The granite mass transgresses the trend of a belt of biotite-quartz-plagioclase gneiss from near one side of the stratigraphically upper part of the gneiss to marble at the base. There are all gradations between porphyroblasts in the biotite-quartz-plagioclase gneiss, porphyroblastic schlieren of the country rock in the granite mass, and uniform granitic augen gneiss. Migmatic facies of the biotite-quartz-plagioclase gneiss are also associated. The granitic gneiss is variable in composition. A syenitic facies is developed locally in mixture with amphibolite. All these phenomena have led to the interpretation that the granitic gneiss is of metasomatic origin. There is also some even-grained granite associated which is inferred to be of direct magmatic origin. There are some bodies of inequigranular granite or granite gneiss intruded as isolated sheets in marble. These may represent remobilized or partly anatectic material, but we have no critical evidence. The solutions effecting the metasomatic development of the augen gneiss are inferred to be related to magmatic masses below.

The structure of the area dominated by igneous rocks, pseudo-igneous rocks, and orthogneisses in the southeastern part (Fig. 15) has been controlled by the anticlinal folds and domes of granoblastic syenite-quartz syenite-older granite orthogneiss that have served as relatively rigid buttresses. The metamorphism and deformation of these rocks along with the Grenville series of beds preceded the emplacement of the younger granitic plutons. The magmas yielding the syenite-quartz syenite-older granite rocks are inferred to have been emplaced as relatively flat-lying sheets or gently dipping phacoliths of the epizone or transitional epizone-mesozone. The northeastern part of the western belt of orthogneiss is a limb of an anticline overturned to the southeast; the southwestern part is a dome. The

northern and eastern anticlines of orthogneiss served as floors for the phacolithic emplacement of the younger granite athough the southern part of the northwest limb of the northern belt of orthogneiss was locally cut out by the younger granite.

There are several synclinal phacoliths of quartz-microcline granitic gneiss. These represent metasomatized biotite-quartz-plagioclase gneiss (Buddington, 1957) in part and in part a quartz-microcline igneous rock of magmatic origin. Much of the metasomatic rock is sillimanitic. The biotite-quartz-plagioclase gneiss is the same type of rock that was replaced to yield the porphyroblastic augen gneiss in the Grenville belt.

The complex in the southeastern part of the area (Fig. 15) is thus composed of tectonoplastic domes and anticlinal cores of granoblastic orthogneiss of an early period; igneous domes, phacoliths and sheets; and pseudophacoliths of metasomatic granite gneiss.

Plutons of Haliburton-Bancroft area, Ontario.—The study of the Haliburton-Bancroft area of Ontario by Adams and Barlow (1910) has made this a classic area for the portrayal of certain aspects of batholithic emplacement. A revised geological map (Ontario Dept. of Mines, Map 1957b) and a revised interpretation of the geology by Hewitt (1956, p. 22–41) have recently been published.

The belt of high-grade metamorphic rocks northwest of the Hastings Basin (Fig. 14) includes marbles and silicated marbles, basic volcanic rocks largely altered to amphibolite schists and gneisses, metagabbro and metadiorite gneiss, paramphibolites, and paragneiss containing sillimanite and garnet. Hewitt describes the batholiths in the high-grade metamorphic terrane as mixtures of granitic material ranging from granitic gneiss to pegmatite intimately injected into and replacing paragneiss and amphibolite. Abundant inclusions and schlieren are present, and gradational hybrid facies of mixed origin are common. Most of the granitic bodies are concordant, and there is much evidence of granitization and metasomatism.

Batholithic Development of Pseudo-igneus Granite in Catazone

Introduction.—The occurrence of replacement pseudo-phacoliths and sheets in the catazone has been discussed. A few examples inferred to represent the development of pseudo-igneous granite as stocks and batholiths will now be considered. Many have been described from the Precambrian, especially the Canadian shield. Early papers advocating the emplacement of batholiths by replacement and recrystallization were those of Quirke (1927) and Quirke and Collins (1930). Some recent examples are those of Harrison (1949), Christie (1953), Robertson (1953), Steven (1957), and Eckelmann and Poldervaart (1957).

Harrison (1949, p. 34–39) described the rocks of the File-Tramping Lakes area, Manitoba, and concluded that granitization has locally affected all volcanic and sedimentary formations in the area and that it has taken place on a regional scale and has locally been intensive enough to produce granite. He infers further, however, that abundant evidence indicates that magmatic granite also existed in large amounts.

Robertson (1953) has described the rocks of the Batty Lake area, Manitoba. He finds that gneissic, granitelike bodies occur in the Batty Lake area as bodies of batholithic size, as stocklike and sill-like bodies, and as pegmatite bodies. Viewed in aerial photographs, the larger bodies exhibit complex to broadly sweeping folds resembling those of sedimentary formations, but in the outcrop they are granodiorites, tonalites, and granites, compositionally, with well-defined foliation and grading imperceptibly into rocks apparently of sedimentary origin. He concludes that "granitization" commences with the development of albite-oligoclase in the sedimentary rocks, producing rocks mapped as "granitized" gneisses, and continues with the later formation of microcline to form bodies of granitoid gneiss that may, in some instances, have become mobile. Robertson suggests that the cause of regional metamorphism and "granitization" in this area is the proximity of magmatic material at depth.

The development of quartz monzonite gneiss and extensive granite pegmatite veining by metasomatism has been described in detail by Steven (1957) from the Precambrian of the Northgate district, Colorado. The country rock is hornblende gneiss, and remnants are abundant in the quartz monzonite gneiss. Metasomatism has been effected by tenuous silica- and alkali-bearing solutions. The gneiss is inferred by Steven to have locally become mobile, moved as a plastic crystalline diapirlike mass, and developed with its foliation in the form of a funnel.

Goldfield-Martin Lake area, Saskatchewan.—The geologic map of the Goldfield-Martin Lake

area in Saskatchewan shows very well the kind of phenomena that have led to the inference of batholithic emplacement by metasomatism. The following description is based on that of Christie (1953), and two selected areas from his map are shown in Figure 17. More than 50 per cent of the Goldfields-Martin Lake map-area is underlain by a complex of granite, granite gneiss, and granitoid gneiss. Christie concludes that the granites have been emplaced mainly by a granitization or replacement process, although various small bodies such as the Mackintosh Bay granite may have been emplaced as a molten magma. The Mackintosh Bay stock is shown in the lower part of area B of Figure 17, and Christie describes it as gneissic with the appearance of having thrust aside the enclosing sedimentary strata during emplacement. The foliation of the granite near the contacts is everywhere parallel to them. Within the stock the foliation has a rough elliptical plan, and lineation indicates a plunge of about 35° SE.

Christie states that in general, although the contacts of granitic rocks and amphibolite are sharp, the contacts with quartzites are commonly gradational over tens, hundreds, or even thousands of feet. Typical coarse-grained pegmatite dikes or sills are rare except in the metasedimentary rocks north and northwest of the Mackintosh Bay granite stock.

The foliation of the granitic rocks near contacts with metasedimentary relics dips gently or moderately but tends to be steep or vertical away from them.

The evidence for emplacement of most of the granitic rocks by granitization is based by Christie largely on gradational zones with quartzite, evidence for a complex series of replacements indicated by interpretation of microtexture, and the lack of displacement of most relict structures. The latter is exemplified by the inclusions outlining a skeletal fold in the upper part of area B of Figure 17.

Quad Creek area, Beartooth Mountains, Montana.—A detailed study of the Quad Creek area of Precambrian age in the Beartooth Mountains has been published by Eckelmann and Poldervaart (1957). Age determinations of these rocks by Gast and Long (1957) based on Rb-Sr place them in general between 2730 and 2800 m.y. The following description is a summary based on the report of Eckelmann and Poldervaart. The Beartooth Mountains form an elongate range with longer axis trending northwest and consist of a core of granitic gneiss flanked by migmatites and metasediments. The historical development is believed to be (1) original deposition of an Archean sedimentary sequence; (2) emplacement of metagabbro and ultramafic intrusions, followed by folding—fold axes strike north-northeast; (3) regional metamorphism and granitization, resulting in a core of granitic gneiss and mantle of migmatites and metasediments with boundaries trending northwest. The last expression of granitization was the production of pegmatites. Eckelmann and Poldervaart believe that their studies indicate in-place formation of granitic gneiss. Fold axes pass continuously and without deflection from the mantle of metasediments and migmatites across the boundary zones into the core of granitic gneiss, although the folds intersect the boundary zone at 40° to 50°. The boundary zone consists of intersecting tongues, migmatites, and granitic gneiss, and these rocks grade into each other along and across the strike. In the boundary zone more resistant rock types persist at definite horizons, continuous with skialiths of similar rocks in granitic gneiss. Throughout, foliation in granitic gneiss and banding in migmatites parallel bedding in metasediments. Growth phenomena shown by zircons of different rocks they believe also indicate autochthonous formation of granitic gneiss at temperatures probably about 500°–600°C. Eckelmann and Poldervaart conclude that granitization was effected by migrating alkaline aqueous solutions during a prolonged Archean cycle of thermal activity. The following statements are also from their description and from a personal communication from Poldervaart. The rocks of the core consist mainly of granitic gneiss, in part showing banding, with many migmatite layers and some metasediments. The zircons are a rounded type with overgrowths and outgrowths. The more homogeneous granitic facies, in particular, have some euhedral zircons. The rocks of a boundary or transition zone comprise migmatites and granitic gneiss with some metasediments. The more nearly homogeneous granitic facies have zircons like those of the core, whereas those of the more inhomogeneous areas are similar to those of the mantle. The rocks of the mantle are mostly migmatites with associated metasediments and some granitic gneiss. Rounded zircons, rounded zircons with outgrowths, and rounded zircons with overgrowths are all present. The first two are about equal in quantity. There thus appears to be a gradation in the transformation of zircons during granitization. The core of the Beartooth block consists predominantly of

FIGURE 17.—TWO AREAS OF PRECAMBRIAN BATHOLITHS

Catazone of Canadian shield from the Goldfield-Martin Lake area, Manitoba, modified from Christie (1953). Granitic gneiss is inferred by Christie to be largely of origin by granitization with relics of folded country rock in area A and upper part of area B. Stock of intrusive granite gneiss with displacement of beds in lower part of area B

pink leucocratic granitic gneiss, with tonalitic gneiss developed toward the migmatitic boundary zone.

The authors emphasize that field relations are critical in establishing the metasomatic hypothesis. Insofar as structure alone is concerned, however, the following alternative interpretation might be posed as a question. Could the pluton have been emplaced between synclinal leaves of country rock as magma wedges that were relatively very thick at the south and thin at the north so that a marked constriction of the magma wedges occurred along the pseudo-discordant boundary of granitic core and mixed rocks? Supplemental granitization would accompany the magma.

Complexity of Precambrian Plutonic Complexes

General.—The Precambrian plutonic complexes of any area of considerable size normally comprise a complex of granitic plutons that have been emplaced in different zones at different times. Anderson, Scholz, and Strobell (1955) have described a Precambrian complex of the Bagdad area, Arizona, where the earliest intrusive members are epizonal plutons of rhyolite and alaskite porphyry, followed by mesozonal plutons (age 1,600 m.y.) in Precambrian schists of intermediate grade of metamorphism. Kalliokoski (1952) has described similar relationships from the Weldon Bay area, Manitoba, where a Precambrian epizonal stock of fine-grained granodiorite with a porphyritic quartz latite border facies is interspersed with younger Precambrian batholithic intrusions that have developed migmatites with adjoining schists appropriate to the mesozone or catazone.

Grenville belt.—The writer has estimated that over a third of the igneous rocks (including orthogneisses) of the Adirondack area of Grenville rocks belong to the syenite-quartz syenite-granite series such as form the cores of tectono-plastic domes and anticlines (Fig. 15). These are inferred to have been emplaced originally in the deeper part of the epizone although much of the rock now belongs to the granulite metamorphic facies. Granite, perhaps 100–200 million years younger, forms 40–50 per cent of the igneous rocks and was emplaced in the catazone.

The Grenville subprovince in the Haliburton-Bancroft area (Fig. 14) includes a belt, the Hastings Basin, about 20 miles wide, within which the rocks are of a low to intermediate grade of metamorphism with stocks having characteristics of the mesozone in contrast to the broad belts on each side of high-grade metamorphic rocks with plutons of the catazone. The rocks of the Hastings Basin consist in part of the Hastings series which is thought by some geologists to be younger than the Grenville series, but by other geologists to be part of the Grenville series. Hewitt (1956, p. 30) writes that

> "The Hastings Basin consists of a terrane of low to intermediate grade of metamorphism, including schists, argillites, well-bedded blue limestones, crystalline limestones, and volcanics. Sedimentary and volcanic structures such as crossbedding, grain gradation and pillows, are frequently well preserved."

The basic lavas frequently belong to the low-grade chlorite facies. Hewitt describes the Deloro granite stock as consisting of a fine- to medium-grained granite with sharp contacts and the McArthurs Mills granite stock as consisting of a massive, coarse-grained granite with irregular shape and discordant structural relations to the country rock. The intrusive plutons in the Hastings series thus have both concordant and discordant contacts, and many have a contact-metamorphic aureole characteristic of the mesozone. The present writer notes that the Marmora metasomatic iron-ore deposit is a fine-grained magnetite-pyroxene-epidote tactite of a type normal for the upper part of the mesozone and dissimilar to the characteristic magnetite-bearing skarns in the Grenville rocks of the catazone.

Colorado Front Range.—Portions of the Precambrian complexes in the Colorado Front Range have been intensively studied and afford an excellent example of their complexity.

The oldest country rocks of the area now consist of high-grade metamorphic biotite-sillimanite schists, quartz-biotite gneiss and schist, quartzite, and hornblende gneiss and amphibolite. The sillimanite-bearing rocks have more aplite and pegmatite.

Plutons of the catazone are well exemplified by the quartz monzonite gneiss (Fig. 18) bodies. Lovering and Goddard (1950, p. 23) describe these rocks as concordant and nearly everywhere parallel to the foliation, with well-developed gneissic structure, closely associated lenticular bodies of pegmatite, and intense *lit-par-lit* injection of inclusions of schist with some assimilation. It may also be noted that a few miles southeast of Central City the quartz monzonite gneiss has typical catazonal phacolithic relationship to a complex isoclinal synclinorial structure within hornblende gneiss.

FIGURE 18.—GEOLOGY OF A PART OF THE FRONT RANGE, COLORADO

Tertiary stocks emplaced in epizone, Silver Plume granite batholith in mesozone, Boulder Creek granite batholith in transitional mesozone-catazone, and quartz monzonite gneiss stocks and phacoliths in catazone. Modified after map by Lovering and Goddard, (1950)

Phacoliths also occur within the schists of the Freeland-Lamartine district to the west described by Harrison and Wells (1956, p. 54) as mostly bodies of biotite-muscovite granite that are generally concordant, although some are sharply discordant. Many of the bodies are hook-shaped and crescent-shaped in their surface exposures and are in the axial regions of folds.

Boos and Boos (1957, p. 2615–2617) state that the probably related Mt. Morrison quartz monzonite gneiss is in part saturated with ill-defined pegmatite; they suggest that it is of granitization (palingenesis and metasomatism) origin.

The Boulder Creek granite (Fig. 18) is described by Lovering and Goddard (1950, p. 25–26) as a quartz monzonite to sodic granite slightly younger and less metamorphosed than the quartz monzonite gneiss previously discussed. The granite is further described to have primary gneissic structure, less well developed but still discernible in the cores of large masses, and locally with abundant inclusions that rarely show much evidence of assimilation. Boos and Boos (1957, p. 2616–2617) state that no other granite of the Front Range has produced so many aplite dikes and sills. They ascribe the granite to a combined magmatic and metasomatic origin. The plutons of Boulder Creek granite are largely comformable but in part break across the foliation of the country rocks. Lovering and Goddard (1950, p. 52) state that the foliation and lineation suggest that the individual plutons are funnel-shaped, enlarge upward, and are accompanied by lateral thrusting. Lovering and Tweto (1953, p. 8–16) on the basis of the orientation of the primary planar foliation and linear structure infer that the batholith was emplaced by rise of magma through a central conduit from which it spread upward parallel to the linear structure that plunges 40°–60°N. The schist along the west edge of the batholith dips under the batholith, but at the north the granite dips under the schist. The foliation of the schist is generally conformable with the contact, and the schist is closely seamed with pegmatite. The present writer suggests that the plutons of this granite may have been emplaced in the transition mesozone-catazone.

The Silver Plume granite plutons (Fig. 18) are inferred by Lovering and Goddard (1950, p. 28) to be younger than the Boulder Creek granite bodies. They state that these granites have a marked tendency to follow faults and cross fractures in schist and gneiss in contrast to the generally concordant habit of the older intrusives. They suggest many local centers of intrusion and that in some places the coalescing of granite masses fed from relatively small scattered conduits at depth has resulted in a composite batholith. Boos and Boos (1957, p. 2616–2618) have suggested that the Silver Plume granite plutons were emplaced by aggressive magmatic stoping.

The Longs Peak-St. Vrain batholith has been correlated by Boos (1934) with the Silver Plume plutons. The present exposures represent the roof portion of a batholith, and Boos describes it as a "pine-tree" type of emplacement effected by lateral spreading and *lit-par-lit* injection of the adjacent and overlying beds with local folding and tilting, although the initial conduits were made by stoping and deep-seated assimilation. There is a gradation shown in the walls of the cirques, 3000–3500 feet high, from schist and gneiss at the top, through almost horizontal layers of schist separating thick sheets of granite, to massive granite with little schist in the lower walls and floors of the cirques.

The Silver Plume granite plutons appear to afford an excellent example where if only the upper portion were seen it might be interpreted as an example of emplacement in the transitional mesozone-catazone, whereas the deeper parts of the pluton have characteristics diagnostic for the normal mesozone.

A few discordant intrusive stocks of Tertiary age and emplaced in the epizone add to the complexity of the Colorado Front Range.

Mackenzie district, Northwest Territories.—The batholithic complexes of the district of Mackenzie, Northwest Territories, Canada, have been described by Henderson (1948) as consisting of both Archean and Proterozoic intrusions, each on a large scale. The Archean batholithic portion intrudes a series of metasediments and metavolcanics but is at many places overlain unconformably by a folded series of Proterozoic formations with basal conglomerates. These beds in turn are intruded by granite batholiths. Both older and younger groups of rocks have members that belong to only a low-grade stage of metamorphism. Henderson has not discussed the mechanics of emplacement of the batholiths. The writer notes, however, that the Archean batholithic complexes in part at least appear to show (Geological Survey of Canada, Map 581A) domal structure and that migmatitic facies are well developed in association with the older intrusions. They may belong to the transi-

tional mesozone-catazone. The Proterozoic intrusions, in part (Geological Survey of Canada, Maps 1024A and 1024B), show cross-cutting relations to the country rock and may belong to the mesozone. In part the Proterozoic granites (Henderson, 1948, p. 47–48) are described as associated with porphyry that locally seems to grade into the granite and to be genetically related to it but in places is cut by the granite with sharp contacts. Henderson writes that no method has been found to distinguish one granite from the other except where critical structural relationships can be determined.

Commentary

General Structural Relationships

A study of the literature on the plutons of North America leads to the following commentary. Plutons emplaced in the epizone, especially the "subvolcanic" plutons with directly associated volcanic rocks, would probably be classed with the atectonic or post-tectonic group, those of the mesozone as post-tectonic and post- or occasionally late-kinematic, and the catazonal plutons, predominantly at least, as syntectonic and syn-kinematic. Also the plutons of the epizone would belong to the "disharmonious" class as defined by Walton (1955, p. 8–11) in which there is a strong contrast between the energy level of the granite and that of the country rock as evidenced by contact-metamorphic effects.

The exposed plutons of the mesozone occur wholly in belts of eugeosynclinal rocks although they are in general post-tectonic. Those of the epizone, however, occur (1) in the eugeosynclinal belts; (2) in belts of miogeosynclinal rocks and structure such as the Sierra Madre Oriental of Mexico (*cf.* Concepcion del Oro, Fig. 6); and (3) in the Colorado, New Mexico, and southern Arizona Rocky Mountain belts surrounding the Colorado plateau where the sediments are of mainland or intracratonic geosynclinal and shelf types and the intrusions coincide with belts of faulting and uplift (Hanover, Santa Rita, and Organ Mountain plutons, New Mexico). The epizonal plutons may also occur in transverse belts such as that of the Boulder-San Juan in Colorado (Fig. 5) and one including and extending northeast from the Boulder batholith in Montana. The Paleozoic and Mesozoic sedimentary beds may locally be so thin that Tertiary intrusions in Precambrian rocks are exposed. Tertiary epizonal plutons of the Oregon Cascade Mountains occur in very gently warped Tertiary lavas and in the Cascade Mountains of Washington in lavas and in folded Tertiary sedimentary beds. The question arises as to whether the epizonal plutons outside the eugeosynclinal belts would pass downward into those of mesozonal type. Ewing and Press state (1957) that the thickness of the crust in the Canadian shield and central Interior Plains is 35 km, whereas it is 40–45 km in the western Great Plains and Basin and Range province and 50–55 km in the Rocky Mountain region. This permits the possibility that the Tertiary plutons of the Basin and Range and Rocky Mountain provinces are connected with deep-seated processes. A mesozonal batholith may also occur in an old orogenic eugeosynclinal structure but may have been emplaced following the development of a miogeosyncline or other type of structure in the same region.

A general discussion of the hypothesis of granite by granitization has been published by Perrin and Roubault (1949) and by Perrin (1954).

Dickson (1958, p. 35) has proposed that magma emplacement may take place by a process he calls "zone melting". This involves crystallization of the base of a column of magma to yield latent heat that is in part transferred by rise of fugitive constituents (mostly H_2O) to the top of the column where melting of the roof is effected. The differential concentration of the fugitive constituents at the top of the magma column arises in consequence of the tendency for such materials to move to zones of lower pressure and lower temperature. The quantitative role of the effectiveness of this mechanism of emplacement remains to be determined. There is the problem of adequate time and appropriate physical conditions. It may be a possible accessory factor under favorable conditions in accentuating differential incorporation of rock with low-melting constituents thereby in turn increasing the potentiality for piecemeal stoping and in increasing the intensity of conditions at the roof of mesozonal batholiths.

Reynolds (1958) has summarized in an attractive manner a stimulating hypothesis that involves a combination of granitization and diapiric rise in deeper levels with movement by fluidization and magma development in the upper levels. She writes (p. 382)

"As a diapir rises, rocks which at a low structural level are obvious migmatites become more and more homogenized by the mechanical kneading caused by superposed movements (Wegmann), and by chemical interchange (with appropriate additions and subtractions, and recrystallization). In this way a migmatite rising in diapir style becomes gradually transformed to nebulite (Sederholm) and eventually to homogeneous granite. If recrystallization outlasts the movement then, just as in salt-diapirs, all traces of the movements will be lost,"

and p. 384

"It is, however, only where granite diapirs have reached the zone of fracture that *evidence* of melting and the birth of acid volcanics has so far been found".

If the writer understands this hypothesis correctly it involves two assumptions for which we must await adequate support: (1) that there is time for a substantial flow of hot matter to diffuse upward through the diapir, and (2) that in the upper zone something is postulated to happen that affords energy to raise the temperature of solid material to the melting point and to supply adequate latent heat of melting to develop magma. The present writer considers it at least equally reasonable to postulate that hot matter diffusing upward from depths would help to liquify granitic material in the regionally hot catazone before that in the much cooler upper zones. The hypothesis of magma from depth to surface has advantages with respect to ease of effecting homogeneity and adaptability to explain the systematic compositional variations of the different units of composite batholiths and their structural details. Efforts to check on such hypotheses as that of Reynolds, however, would doubtless lead us to new insights.

The epizonal stocks and batholiths have been emplaced at one extreme by columnar subsidence with a 360-degree ring fracture (Ossipee pluton, New Hampshire) and at another extreme by piecemeal stoping of angular blocks (eastern part of the pluton in Northgate district, Colorado). Subsidence of blocks for most plutons probably involves both arc and intersecting angular block fracturing in varying degrees. The alternative development of columnar subsidence or of piecemeal stoping is not related to depth. One factor in aggressive piecemeal stoping as contrasted with permissive subsidence may be the predominance of a tendency for the magma to lift the roof with consequent breaking and subsidence. The problem needs study.

Predominance of Mesozonal Batholiths in Plutonic Complexes

The tremendous total volume of batholiths with their directly associated rocks of high-grade metamorphism in plutonic complexes of orogenic belts predisposes one to think of the complexes predominantly in terms of very deep-seated erosion and of batholithic emplacement in the catazone. This, however, is only partly true, for most of the batholiths of most orogenic belts were emplaced in the mesozone (including the transition mesozone-catazone).

There is only one well-authenticated *great* belt of uniformly high-grade metamorphic rocks with associated intrusives in the whole Canadian shield. This is the belt of Grenville-type rocks that extends for over 1000 miles from Labrador to Pennsylvania and is more than 250–350 miles wide. This belt in part has rocks that belong to the granulite facies and is also characterized throughout by the presence of great anorthositic plutons. The ages of the granitic intrusives insofar as now determined range between about 900 and 1100 m.y. At least part of the belt of Precambrian rocks in the Rocky Mountains such as that in Montana, Wyoming, and Colorado may be analogous to the Grenville belt. Granitic rocks with ages of 2700–2800 m.y. and anorthosite bodies occur in this belt.

The batholiths of such provinces as the following, however, were predominantly emplaced in the mesozone: the Keewatin province with a width of more than 250 miles and with rocks intruded by granite pegmatite with ages of 2,500 m.y.; the Yellowknife belt, Northwest Territories, with pegmatites at least 1850 m.y. old; the Colorado Front Range with some granite plutons of about 1000 m.y. age; the belt about 200 miles wide across Newfoundland with plutons of Acadian age; and the zone of Jura-Cretaceous batholiths about 350 miles wide in Alaska and British Columbia. The intensity of regional metamorphism as indicated by rocks farthest from the major intrusives is prevailingly that of the greenschist facies with local zones in the staurolite-kyanite subfacies. The sillimanite facies is generally restricted to zones of rock adjacent to the major plutons or complex of plutons.

Criteria for Large-Scale Granitization

Several examples have been described in the literature in which it has been postulated that

large-scale granitization has resulted in batholithic masses. One of the difficulties in proving granitization is that nearly all criteria are subject to alternative interpretations. Much of the rock involved is a leucogranite of a composition approaching that of the experimentally determined ratio for the major minerals concerned at minimum temperatures with H_2O in solution. A satisfactory hypothesis as to why replacement of varied rocks in an open system by alkalic-siliceous solutions should result in leucogranite approaching the composition experimentally determined to be that of the cotectic has yet to be offered. Overgrowths and outgrowths on rounded zircons may develop in contaminated magma as well as during granitization of metasediments in place.

The problem of the proper interpretation of the significance of long thin layers of country rock occurring either as linear slabs or outlining skeletal folds is an old one. (*Cf.* Lawson, 1894, p. 296.) A skeletal fold outlined by metalimestone slabs in the Harney peak batholith is interpreted as xenolithic in intrusive granite by Runner (1943, p. 449–453), whereas a long thin metalimestone layer in granite on the border of the Clare River syncline is inferred by Ambrose and Burns (1956) to necessitate an origin as a relic in granite gneiss of granitization origin. The metasedimentary rocks outlining skeletal folds in the Goldfield-Martin Lake area are also inferred by Christie (1953) to be relics in a batholith of granite gneiss of granitization origin, although the present writer would note that some phacolithic magma emplacement, if not indicated, at least does not seem precluded by the relationships shown on the map (Fig. 17). Folded amphibolite layers and thin amphibolite layers in granite phacoliths of the Northwest Adirondacks are interpreted by Buddington (1929) as xenoliths in granite of magmatic origin, whereas skeletal folds outlined by layers of hornblende gneiss near Northgate, Colorado are explained by Steven (1957) as relics residual in quartz monzonite of granitization origin. Many recent authors emphasize a skialithic as contrasted with a xenolithic origin. Extensive thin layers of country rock do however occur in igneous sills (Eckel, *et al.*, 1949, Pl. 2), laccoliths, and stocks (Murthy, 1957, p. 94). The conditions of emplacement in the catazone are intense and syntectonic, and it seems probable that conformable emplacement would be facilitated. Metasedimentary inclusions in the form of relic folds or skeletal folds in granite gneiss are not necessarily "skialiths" but may be thought of as arising from a complex phacolithic mechanism of magma emplacement into country rock that has complex folds, boudinage structure, and formations much thickened and thinned by differential plastic flowage. It is expectable that the magma will be accompanied by some granitization, partial fluxing of the lowest-melting constituents of the country rock, and hybridization. The shredded ends of some layers may be due to being squeezed or pulled apart during plastic flowage as well as to irregular replacement. It thus seems highly probable that metasedimentary rocks as layers or skeletal folds in granite or granite gneiss may be either of xenolithic origin in magmatic granite or of skialithic origin in metasomatic granite gneiss.

It has been argued that some batholithic emplacement by granitization has been accompanied by inflation with outward deformation of the walls as the result of introduction of new material. Barth (1947, p. 181) infers that the Birkeland, Norway, batholith with conformable walls is a "petroblast" developed by the introduction of new material as a "cloud of ichor or migrating ions". Oertel (1955, p. 45) describes the Loch Doon stock in Scotland as having expanded its volume by 34 per cent and (p. 81) "Der Pluton ist durch Metamorphose unter Stoffzufuhr aus pneumatolytischen Lösungen und durch metasomatische stoffwanderung entstanden". The Loch Doon pluton has discordant contacts for much of its border. To the writer's knowledge the concept of expansion of the walls as a result of granitization has not yet been advocated for any North American pluton. This is perhaps because hundreds of examples of mineral deposits have been studied in which there has been introduction of new material, but little or no evidence for inflation in consequence of it has been reported.

Emplacement of Plutons in Epizone and Mesozone

Lava flows, acknowledged by all to be of magmatic derivation, may be considered an observable large (as contrasted with the size of an ion) base of known origin from which to extrapolate to a corresponding magmatic origin for most plutons of the epizone.

The common occurrence of homophanous structure, the common local development of miarolitic or aphanitic texture, and the inferred genetic relationship to lavas of similar composition associated in time and space all in-

dicate that the Tertiary plutons were emplaced as magmas, largely or wholly fluid. "Far-travelled" xenoliths from depth and absence of flow structure in the enclosing rock of some plutons necessitate a fluid mode of transfer from depth. The magma of Tertiary plutons was, in the initial stages, fluid enough to yield lava flows. At later stages, after rise to higher cooler levels in the accumulated lava pile, loss of volatiles at lower pressures and partial crystallization would occur, and the magma would become viscous enough to "set" before reaching the surface *en masse*.

Many geologists have emphasized the development of a schistosity that is steeply dipping, often with subvertical lineation, in both peripheral country rock and in border facies of plutons, such as most of those of the mesozone and many of the transitional epizone-mesozone. Because of this they have inferred that the invading material had to be a highly viscous or a diapirlike mass, partly or largely crystallized, rising upward and dragging its walls. This is probably true for much of the quartz diorite facies that forms the outer part of many plutons. Such quartz diorite is reasonably interpreted as the product of incorporation of country rock by a more specifically granitic magma and might therefore be expected to be partly crystalline. Again, successive central intrusion of magma could produce inflation, deformation, and upward drag of partly to largely consolidated earlier facies. In some plutons of the mesozone, upward movement in the border zones persisted through the very last stages of consolidation and even into the solid state.

Such evidence for viscous magma in the border zones, however, does not preclude the possibility that even initial stages of magma emplacement in the mesozone may locally have been freely fluid, and it has no necessary bearing on the later intrusion of the cores.

Even conformable schistose structure in the contact zones of mesozonal plutons need not always indicate development in consequence of emplacement of viscous magma. Durrell (1940) made a systematic study of contact metamorphism in the southern Sierra Nevada and emphasizes that, in contact zones with granite, metasedimentary phyllites and schists may merely coarsen in grain but retain the original foliated structure, a mimetic inheritance. This means that if the material of a pluton of the mesozone were a fluid magma in the early stages we should not necessarily expect a hornfels to be formed from metasedimentary phyllites, and if formed it might disappear subsequently by stoping. It may also be noted that hornfels, as distinguished from schist, does occur in the wall rock of some mesozonal plutons. In part, however, early hornfels may itself be deformed at later stages of magma emplacement.

Much of the gneissoid granite does not show the amount of crushing and protoclastic structure that would be expected if flowage occurred at a late stage of consolidation. Freely suspended crystals in an early stage of crystallization may be oriented by flowage, and this orientation may be preserved and inherited by subsequent overgrowth and control of crystallization by the early fabric.

It seems probable that much, if not most, of the magma that yielded the rocks of the mesozonal plutons was predominantly liquid at the time of its emplacement.

There is good evidence that lavas and locally some hypabyssal plutons crystallized with some minerals characteristic of higher temperatures than those of their plutonic equivalents (Tuttle and Keith, 1954; Muir and Smith, 1956; Buddington *et al.*, 1955, p. 519–522). Most of the plutons, however, especially the larger ones, will have crystallized in the presence of at least part of their volatiles, will therefore have remained partly fluid for a long time down to temperatures lower than those of lavas, and any initial high-temperature minerals will have undergone recrystallization at lower temperatures. The plutons in the epizone, and their inferred relationships to those of greater depth, necessitate that the fluid magma that formed them could have risen from source to surface in a relatively short time—a small fraction of the length of time assigned to a geologic period. Otherwise the magma would have frozen en route.

A hypothesis is that autochthonous and parautochthonous batholiths are metasomatic in origin, wholly or predominantly solid, and arose in and ascended from zones now exposed in the more deeply eroded areas. This raises a problem if we also assume, as is here done, that most of the plutons emplaced in the epizone and in part in the mesozone were predominantly liquid magmatic. The foregoing hypotheses taken together would necessitate that the plutonic mass became more liquid as it rose into cooler levels and that it left a concentrated residuum of resistant type of rocks in their source area, the catazone. Rise into lower-pressure zones, chemical reactions, and increase in volatiles in the upper part of a magma

column (Kennedy, 1955) would tend to increase fluidity, but it remains to be shown that these factors are adequate to meet the requirements. The development and rise of granitic magma out of the roots of eugeosynclincal materials would presumably leave behind a series of rocks composed predominantly of garnet amphibolite and magnesian pyroxene-calcic plagioclase granulite but with some other refractory materials. This complex would be appropriately consistent with the seismic data for rocks above the M discontinuity in the lower part of the crust not now exposed, but there is no satisfactory evidence that there is a concentration of "resistates" in the now-exposed portions of the catazone. If erosion has only locally exposed levels deeper than about 12 miles in the earth's crust, as seems probable, then we conclude that most magma usually came from levels deeper than most now at the surface.

The apparent dominance of lineation, insofar as flowage structures do occur, in plutons of the epizone and the dominance of planar foliation, with or without lineation, in the plutons of the mesozone correlate with the differences in mechanics of emplacement and different conditions of consolidation and flow in the two zones. Lineation alone appears to be related to an early fluid stage followed by continued crystallization in quiet. In the mesozone continued movement during a protracted intermediate period of crystallization permits the development of planar structure in some parts of the pluton.

There appears to be good evidence that some of the plutons of the mesozone had extensive roofs and could not have been continuous with plutons of the epizone unless through relatively small connecting channels. The plutons of the mesozone and epizone locally overlap one or more of their borders as though overriding them, but in general the evidence for an extensive floor is lacking.

The present data do not preclude the possibility, however, that the plutons of the epizone, at least in part, enlarge downward and are continuous with plutons of the mesozone. If the emplacement of the latter were in substantial part effected by crowding aside of the walls then the possibility would exist for emplacement of magma in the epizone through foundering of crustal blocks into magma below. A domical-planar or arch-linear structure such as occurs in some plutons of the mesozone could form at a late stage in consolidation and would not necessarily indicate a roof of original country rock at time of consolidation.

The mechanics of emplacement of plutons in the epizone as a consequence of alternating magma rise with accompanying pressure effects and magma relaxation with accompanying appropriate structural collapse of roof and walls have been discussed by Anderson (1936) and by Billings (1945, p. 53–55; 1947, p. 279–288).

In the mesozone, yielding of the walls by plastic flowage may be expected to be greater with depth. This will commonly result in outward-flaring walls, distention of the roof, and the potentiality for collapse of local portions of the roof over the border zones of the underlying magma. This may in part explain the occurrence of both discordant and concordant boundaries so characteristic of plutons of the mesozone.

It is recognized that replacement may occur locally with sharp and even discordant contacts. An origin by mechanical rather than chemical processes, however, seems the best interpretation for most contacts of plutons in the epizone, and the similarity of character and probable history indicates a similar mechanical origin for most sharp discordant contacts of plutons in the deeper zones.

The writer finds no evidence for postulating a discontinuity between the compositions, textures, internal structures, or mechanics of emplacement of plutons in the epizone and those of the mesozone. There are plutons with intermediate characteristics that suggest a series of gradational changes from one to the other.

The concept of the development of migmamagma with schlierenlike structure at the source seems reasonable, but its rise and emplacement "as such" does not fit the homophanous core of the plutons of the mesozone and those of the epizone.

The North American literature of the past 25 years appears to be based on the assumption that the best theory, as of the present, for emplacement of plutons in the epizone is one of block foundering in, or some kind of stoping by, magma as a major factor. After half a century, however, the stoping hypothesis still lacks verification in the sense that we do not have desirable supporting evidence of sunken blocks in the plutons of deeper levels. Unless such blocks have been indistinguishably incorporated in magma, or reworked and metasomatized into new granites at depth, or have sunk to very great depths, we might expect to find more evidence of floored plutons than has been reported.

Three major factors of emplacement of plutons in the mesozone are inferred to be stoping or block foundering, crowding aside of the walls, and uplift of the roof. The sideward expansion may in part result in plastic flowage of country rock upward and downward. Additional factors are incorporation of country rock and metasomatism of wall rock. The importance of each factor varies with the particular example. If the tonalities of the batholith of Southern California are inferred to result from incorporation of gabbro by granodiorite magma then gabbroic material may be inferred to be equivalent to about half of the tonalite that forms 63 per cent of the area now occupied by the batholith. This would make the problem of emplacement of the batholith one of how so large a volume of the initial gabbro was introduced as well as of how so great a mass of granodiorite was emplaced. Similarly at least 10 per cent of the problem of emplacement of the Coast Range batholith of Alaska and British Columbia could be related to incorporation of mafic rocks. Most of the mafic rocks in orogens, however, are lava flows and intrusive diabase, dolerite, or gabbro sheets emplaced under conditions of the epizone previous to major deformations.

A great variety of structures associated with plutons of the mesozone have been cited as consistent with formation by upward movement of magma. Such structures within the plutons are subvertical foliation and lineation in border facies, marginal fissures with pegmatite or aplite, marginal upthrusts, radial dikes, and schlieren domes; structures in the country rock near the pluton may be increase in dip of foliation or of slaty cleavage or of the plunge of lineation, subvertical lineation and subvertical secondary fold axes of plastic flowage origin, slip cleavage roughly similar in strike to the periphery but dipping outward with the lower schist layers moving up relative to the overlying layers, and development of domical foliation in the roof.

Structures consistent with outward expansion effected by the pluton are deformation of beds into partial conformity with the periphery, intensification of folding, and in part the intensification of planar foliation in the border facies of the pluton itself.

All discordant structures need not necessarily mean stoping, for expansion effects of the pluton may result in pulling portions of the country rock apart; in many examples, however, this possibility is not of sufficient magnitude to satisfy the actual relationships.

Emplacement of Plutons in Catazone

If the writer has correctly interpreted the literature, then most, perhaps all, of the plutons of the catazone were emplaced under synkinematic conditions. The roof portions of a number of batholiths of the mesozone are similar to those of plutons emplaced in the catazone, but such conformable emplacement in the mesozone does not, in part at least, appear to be related necessarily to regional tectonic forces. Such plutons may be intermediate between those typical of the mesozones and those characteristic of the catazone. The extent to which plutons of the catazone are due to metasomatism or anatexis is yet to be definitely determined. It is logical to assume that at their source granitic masses would as a result of anatexis and rise of temperature become mobile and rise as diapirs or as "migma-magma", but the extent to which source areas are now exposed is most problematical.

Marshall and Narain (1954, p. 73) have postulated that the negative gravity anomalies over granite batholiths, of a type here inferred to belong to the mesozone, are due to "granite roots", to extension of the granite pluton to depth, rather than due only to density contrasts between granite and country rock near the present surface. Presumably this could mean continuity of plutons of the mesozone with those of the catazone. Biehler and Bonini (1958) have concluded that, if reasonable assumptions are made for the probable geology and density distribution of the region of the Boulder batholith, it follows that a granite mass roughly with a plano-concave cross section and a depth not much less than and not much more than 10 miles will closely satisfy the residual negative bouguer anomaly. An additional narrow root could also be present.

Grout (1945, p. 276–278) on the basis of some experimental evidence suggests that large intrusives that rise from great depths may have only roots or a series of roots and that they may ascend along part of their route because some of the overlying rocks become so reduced in viscosity that they move aside and down along the sides in a mobile contact zone. There may be accompanying distention and sideward flow in the roof during emplacement. Such a mechanism of intrusion would permit an effective discontinuity in the size of

the areal cross section of batholiths in the deeper part of the mesozone with the areal cross section of their feeders from the catazone. The shape of the intrusive mass would be streamlined and comparable to the shape of salt diapirs with pinched-off roots. The lower part of such bodies should have inward dips. Symmetric funnel-shaped plutons such as the Loon Lake (Fig. 14) are few, but a number of deep-seated plutons such as the Cheddar batholith (Fig. 14) and the southwest side of a part of the Coast Range batholith are asymmetric in cross section and bordered on one side by inward-dipping schists. The problem of batholithic roots in the transition zone between the mesozone and catazone and in the catazone deserve more detailed study.

The details of the interrelations of plutons of the catazone to those of the mesozone and of those of the mesozone to those of the epizone remain as problems. A tentative schematic diagram of relationships is shown in Figure 19.

A phacolithic mechanism of emplacement seems to be a major kind in the catazone, and often phacoliths of both igneous and of metasomatic origin are reported to be associated. Many xenolithic domal batholiths may also, in part at least, result from a phacolithic mechanism of emplacement, usually igeneous but in part metasomatic.

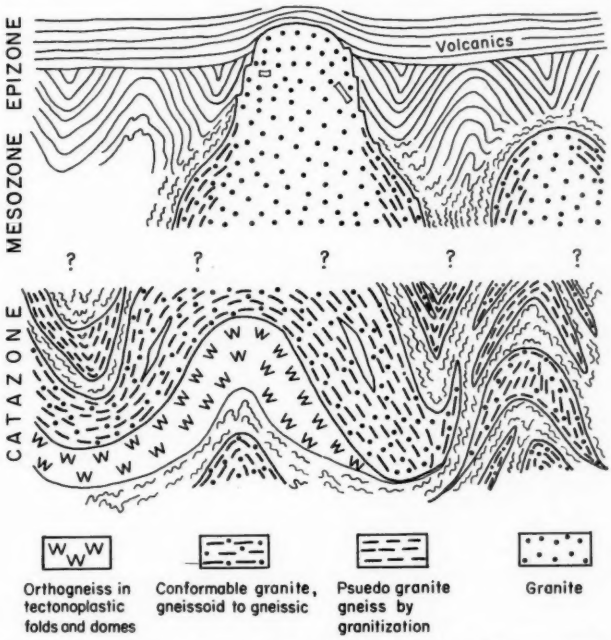


FIGURE 19.—SCHEMATIC SKETCH SHOWING POSSIBLE STRUCTURAL RELATIONSHIPS OF PLUTONS IN EPIZONE, MESOZONE, AND CATAZONE

Question is left open as to whether batholiths of mesozone enlarge downward in continuity with those of catazone or whether they have roots

Age determinations permit the inference that the youngest plutons of the catazone with extensively developed migmatities are about 100 m.y. old and that plutons of the epizone may be at least as old as 1.65 b.y. and probably much older. Plutons of the mesozone range in age from slightly less than 100 m.y. to those of the Keewatin belt of the Canadian shield which are 2.5 b.y. or older.

Origin of Granitic Magma

"We must still entertain the hypothesis that most granites have been produced throughout geologic time by differentiation of basic (basaltic) magma, in part somewhat modified in its course from depth". (Bowen, 1948, p. 87).

The role of metasedimentary material as the prime source of most granitic magma is now emphasized far more than is implied in the statement of Bowen cited above. There appears to be a tendency at the present time to start with the assumption of at least two major magmas—one, the granitic derived from the sialic part of the crust, the other, the basaltic from deeper down, probably in the mantle, or beneath the continents from an eclogite root.

Graywacke forms a large part of eugeosynclinal sediments. It would with increasing melting yield successively a little true granite and then a trondhjemitic magma. The latter by reaction with associated basalts would result in a tonalitic magma. Partial melting of an illitic type of clay has been shown by Winkler (1957, p. 57–58) to yield an exceptionally potassium-rich leucogranitic magma. The hypothesis that the lowest part of the sial contains some primordial granitic material differentiated from basaltic magma however is reasonable and has not as yet been precluded, especially for the early stages of geologic history. Remelting of such primordial granite would, of course, yield granite magma directly. An andesitic magma may form by partial melting of a gabbroic or eclogitic continental substratum or essentially by incorporation of graywacke in basaltic magma.

Basaltic magma may yield basalt or gabbro directly by consolidation; dioritic-andesitic magma by assimilation of sialic material or by mixing of femic and salic magma; and ultramafic, anorthositic, monzonitic, granophyric, and other subordinate facies by differentiation. The granitic magma may yield granites directly; minor diorite by incorporation or metasomatism of mafic rock; and mobile quartz dioritic or other intermediate kinds of magma by incorporation of graywacke and earlier basalt flows or gabbro plutons. The quartz dioritic magmas may in turn yield granodiorite, quartz monzonite, and new granite magma by differentiation. The initial volume of gabbro emplaced in the mesozone and epizone must have been much larger than that now represented by exposure. Much of it foundered in later intrusive granitic magma and was incorporated to reappear in the modified facies such as quartz diorite.

Read (1951, p. 22) has made a tentative suggestion that "we seek the ultimate source of the granitising fluids in crystallising simatic material below the site of the geosyncline." Adoption of such a hypothesis has a number of significant consequences. Simatic material in crystallizing at depth slowly over a long time may be expected to undergo fractional crystallization and differentiation to yield directly magmatic monzonitic to dioritic differentiates (especially if magma is undersaturated) or magmatic granitic differentiates (if oversaturated). The released granitizing fluids, either magma, gas ions, or all three may be expected to modify the material in the lowest part of the geosyncline and add to or develop granitic magma. The effect of pressure in raising the temperature of melting is not adequate to prevent a rise of temperature and pneumatolytic fluids from fluxing granitic material at the base of the sialic part of the crust rather than higher up. The source zone for the plutons would therefore not be expected to be exposed.

Tuttle (1955) has estimated that with a geothermal gradient of 30°C. per km partial melting of a geosynclinal prism of sediments might start to yield a biotitic granitic magma with a temperature of about 640°C. at a depth of 21 km and that complete melting with about 2 per cent H_2O could occur at about 31 km. With a gradient of 40°C. per km incipient melting could occur at a depth as shallow as 15 km.

The usual order of intrusion—gabbro, quartz diorite, granodiorite, quartz monzonite, and granite—in composite plutons is one that corresponds to the order theoretically expectable as a result of magmatic differentiation or alternatively to that of decreasing temperatures. A speculative hypothesis to explain this order might be as follows. The early rise of basaltic magma directly yields gabbro plutons, diabase sheets, and basaltic lavas; basaltic magma with incorportation of sial leads to andesitic lavas and minor diorite plutons. Subsidiary effects of the development and rise of basaltic magma and its derivatives are accentuation of the rise of the isogeotherms and fluxing in the lowest part of the sial. As the isogeotherms rise through the deep sial early formed interstitial low-melting granitic fluids work upward, react with country rock in part, and result in a differentiated domal column ranging upward in composition from residual refractory materials at the base through quartz dioritic and granodioritic facies to granite at the top. Eventually the continued rise of the isogeotherms results in sufficient melting of the lower portion of the column—either the quartz dioritic or granodioritic facies—so that

it rises as a whole followed successively by melting and rise of the overlying materials. Granodioritic magma may in turn react with mafic material on its upward flow to yield quartz diorite. Later granitic magma may rise through a sheath of the earlier intrusives. Other hypotheses are desirable.

The variation in ratio of different kinds of igneous rock in the different zones needs study.

The plutons of the epizone may be predominantly granodiorite, quartz monzonite, and granite. The tonalitic facies in general appear to form a larger percentage of the rocks in the plutons of the mesozone than in those of the epizone. Quartz monzonite, granite, and leucogranite or alaskite are far more common among the members of the granite family in certain belts of the catazone than in the mesozone (Daly, 1914, p. 60; Osborne, 1956). In particular, andesine-quartz diorite apparently is relatively subordinate in these belts. Andesine and labradorite anorthosite and gabbroic anorthosite of the types found in massifs and independent sheets are possibly almost exclusively in belts of the catazone. Assuming the foregoing relationships are correct, although we do need quantitative data to substantiate them, some suggestions as to their origin may be offered as bases for study. Is the restriction of the types of anorthosite mentioned to the catazone the result of the necessity for the kind of environment which by acting as a plastic envelope (the country rock is often marble) under high pressure permits the retention of the high volatile content essential to keep the equivalent magma fluid and of gabbroic anorthositic or anorthositic composition, or is it a phenomenon to be correlated with greater age, or both? A favorable home for quartz diorite is the mesozone. Is this because the quartz diorite magma originates largely through reaction of more alkalic granitic magmas with mafic rocks, thus losing fluidity and to a substantial extent not rising above the mesozone? Is the predominance of granodiorite and granite relative to quartz diorite in the epizone the consequences of equivalent magmas being the lightest types and fluid at relatively low magmatic temperatures because of volatile content and their lower melting intervals? Why the predominance of granite in certain catazonal belts? One answer might be, "They are granitization products". But the writer is not convinced that this is the whole answer because magmatic mesoperthite granite bulks large in the Adirondack belt of catazonal rocks.

Problem of Volcanic and Plutonic Associations

One of the most critical problems is whether or not our present knowledge indicates, or is consistent with, the hypothesis that there is a direct relationship between salic volcanic rocks, aphanitic or porphyritic intrusions, and granitoid plutons.

Kennedy (Kennedy and Anderson, 1938) has made a sharp distinction between *volcanic* and *plutonic* associations with respect to igneous rocks. He postulates that the *volcanic associations* include not only lava flows and directly related vent intrusions but also such intrusions as the great sill swarms of the Karroo, South Africa, the Palisades sill of New Jersey, and even the great sheets such as the Bushveld igneous complex of the Central Transvaal, South Africa, all of which are in nonorogenic areas and intimately associated with volcanic phenomena. *Plutonic* associations on the other hand he suggests appear to be limited to orogenic regions and consist almost entirely of granodiorite and granite together with smaller amounts of their associated predominantly hornblendic, basic, ultrabasic, and lamprophyric types, while typical gabbros are characteristically rare or absent. He further states that volcanic associations, on the contrary, are overwhelmingly basic and are composed mainly of basaltic magma or of rock types belonging to a basaltic line of descent. He concludes (1938, p. 30) that

> "Altogether, there does not appear to be any very direct evidence to indicate a close connection between plutonic activity and volcanicity"

and (1948, p. 2–3) that

> "there is a universal absence of lavas belonging to a period contemporaneous with the rise of batholithic intrusions to their highest levels in the crust."

A recent discussion of the problem has been given by Raguin (1957, p. 185–199). He refers to subvolcanic granite masses as truly very special and exceptional and moreover ambiguous in interpretation. He attributes to E. Suess the development of the concepts that successively deeper denudated levels reveal lava flows, hypabyssal porphyry intrusions, and grained plutonic bodies of similar composition but different texture and that all are

genetically related. He also presents a discussion of an opposite philosophy that envisages the foregoing concepts as seductive but deceiving and that interprets the association of volcanic rocks and major plutons in the earth's crust to have no direct relationship. Some proposed objections to the Suess concepts are that the succession in plutonic rocks is from basic to acid but in volcanic rocks from acid to basic, irregular or recurrent; volcanic rocks may occur independent of plutonic rocks, and *vice versa*; volcanism is related to periods of fracturing of the crust, plutonism to periods of folding; plutonism occurs after vulcanism; a true volcano has never been observed to rise from a plutonic mass; and identities such as volcanic and plutonic quartz porphyries are only a phenomenon of convergence. Raguin concludes that the problem of the relationship of vulcanism to plutonism is still unsolved.

The ideas of Kennedy have been criticized by Tyrrell (1955, p. 420) who writes

> "The lava series ranging from pyroxene andesite to rhyolite, therefore, has the same chemical composition, the same geological and geographical distribution, the same tectonic environment, and appears at the same stage of the tectono-igneous cycle as the plutonic series ranging from quartz diorite to granite. If the latter belongs to the plutonic association there seems to be no escape from the conclusion that the andesite-dacite rhyolite series likewise does . . . . The writer suggests that the whole trouble with plutonic and volcanic associations is that they are wrongly named."

The many citations (21) in this review demonstrate that it is normal for volcanic rocks of equivalent composition to be associated in space, time, and tectonics with plutons emplaced in the epizone. Many granitic bodies that have been called plutonic because of their medium to coarse grain and their batholithic size are not plutons in the sense of deep-seated emplacement. Exceptionally cogent examples that provide a clear demonstration of the succession of magmatic activity from volcanism to high-level granite emplacement have been described from Northern Nigeria by Jacobson, MacLeod, and Black (1958, p. 7). Here are about 40 granite complexes in a belt about 270 miles long and up to 100 miles wide. The total area of granite is about 2000 square miles, and there is about 500 additional square miles of rhyolite of similar chemical composition and age. The rhyolite furthermore is almost wholly confined within the granite ring complexes. The granite plutons are up to 285 square miles in area. If there were only about 3 times as many complexes, each with about 3 times the area, in the mesozone beneath this belt, it would mean a continuous great batholith, 270 miles long with an average width of 65 miles.

Some of the very small plutons of the epizone may be granitic, granophyric, or monzonitic differentiates of basaltic magma bodies located somewhat below. But it seems essential that most of the salic lava flows and stocks and all the batholiths of the epizone originated from granitic magma of deep-seated origin.

A diversity of succession in lava sequences can reasonably be interpreted in terms of successive pulses of basaltic or andesitic magma from depths and magmas of the rhyolite, rhyodacite, dellenite, dacite group from epizonal plutons. It is also probable that some of the epizonal dikes of granitic composition came directly from great depth rather than from epizonal plutons. In summary, the mafic rocks are predominantly extruded as lavas or emplaced in the epizone, whereas the felsic rocks, although including lava flows and many related plutons emplaced in the epizone, are by volume per cent largely emplaced in the mesozone and catazone. If the granite originated as a differentiate of gabbroic magma in the mesozone or catazone, at a level above the source of the gabbroic magma itself, then bodies of gabbro at least 10 times as large as the granite plutons should be common in the mesozone or catazone of the orogens. Such bodies do not occur in appropriate volume in these zones as now exposed.

Conclusion

The foregoing survey shows that the authors who have reported on detailed structural studies of stocks and batholiths in North America have reasoned that granitization only occasionally has played a role in the mechanics of emplacement of plutons in the epizone, has been of subordinate significance (one author excepted) in the mesozone, but has played a major although not necessarily a greatly preponderant part in the catazone. Otherwise the reliance has been on magma emplacement. One might also conclude from such a survey, however, that the unity of agreement in interpretation has been far too great to be healthy for the optimum advance of our understanding. Hypotheses, in general, as to the respective roles of magma and of metasomatism in the emplacement of granitic plutons are conflicting,

and the problem remains one demanding critical studies and more dependable criteria.

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ION EXCHANGE IN CLAYS AND OTHER MINERALS

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ABSTRACT

Ion exchange in clays and other minerals is dependent on the crystalline structure of the mineral and on the chemical composition of any solution in contact with the mineral. The structures of clay minerals and zeolites are briefly described to provide a background for the discussion of their ion-exchange reactions. Ion exchange in these minerals is a reversible chemical reaction that takes place between ions held near a mineral surface by unbalanced electrical charges within the mineral framework and ions in a solution in contact with the mineral. Generally the excess charge on the mineral is negative, and it attracts cations from the solution to neutralize this charge. The chemical reactions in ion exchange follow the law of mass action, but the reactions are restricted by the number of exchange sites on the mineral and by the strength of the bonding of the exchangeable cations to the mineral surface. Titration of H-clays with bases shows that montmorillonites and "illites" behave like a mixture of two or three different acids, whereas kaolinite, with an indefinite number of exchange sites, behaves like an indefinite number of acids.

Ion-exchange capacity is measured in chemical equivalents of base adsorbed at pH 7. Each clay mineral has a range of exchange capacities because of differences in structure and in chemical composition. The ranges (in milliequivalents per 100 grams) are kaolinite, 3–15; halloysite ($2H_2O$), 5–10; halloysite ($4H_2O$), 40–50; montmorillonite, 70–100; "illite," 10–40; vermiculite, 100–150; glauconite, 11–20; attapulgite, 20–30; and allophane, 70. The common metallic cations found in exchange positions in clay minerals are Ca^{+2}, Mg^{+2}, Na^{+}, and K^{+}. At low pH values H^{+} replaces other cations. The order of replaceability of the common cations has been found to be:

$$Li^{+} < Na^{+} < K^{+} < Rb^{+} < Cs^{+} \text{ and } Mg^{+2} < Ca^{+2} < Sr^{+2} < Ba^{+2}.$$

Bivalent cations enter the exchange sites preferentially to univalent cations. The common exchangeable cation in most clay minerals in soils is Ca^{+2}.

Other exchange phenomena discussed are anion exchange, fixation of cations and anions by clay minerals, effect of environment on cation exchange, and the exchange capacity of zeolites, of rocks, of other minerals, of organic matter and organic complexes, and of amorphous mineral material.

SOMMAIRE

Les échanges d'ions, dans les argiles et autres minéraux, dépendent de la structure cristalline du minéral et de la composition chimique de la solution en contact avec lui. Les structures des minéraux argileux et des zéolites sont brièvement décrites, en vue de fournir une base pour la discussion de leurs réactions d'échange. Un échange d'ions est, dans ces minéraux, une réaction chimique réversible, se produisant entre des ions retenus à la surface du minéral, par des charges électriques non équilibrées du réseau cristallin, et des ions d'une solution en contact avec le minéral. En général, la charge en excès sur le minéral est négative et les cations de la solution sont attirés pour la neutraliser. Les réactions chimiques, dans les échanges d'ions, suivent la loi d'action de masse, mais elles sont limitées par le nombre de positions d'échange sur le minéral et par la force de liaison des cations échangeables à la surface du minéral. Le titrage des argiles-H, à l'aide de bases, montre que les montmorillonites et les "illites" se comportent comme un mélange de deux ou trois acides différents, tandis que la kaolinite, avec un nombre indéfini de positions d'échange, se comporte comme un mélange d'un nombre indéfini d'acides.

La capacité d'échange d'ions se mesure en équivalents chimiques de base absorbée à un pH égal à 7. Chaque minéral argileux présente un intervalle de capacité d'échange, dû à des différences de structure et de composition chimique. Les intervalles (en milliéquivalents pour 100 g) sont: kaolinite, 3–15; halloysite ($2H_2O$), 5–10; halloysite ($4H_2O$), 40–50; montmorillonite, 70–100; "illite", 10–40; vermiculite, 100–150; glauconite, 11–20; attapulgite, 20–30; et allophane, 70. Les cations métalliques se trouvant couramment dans les positions d'échange des minéraux argileux sont: Ca^{+2}, Mg^{+2}, Na^{+} et K^{+}. Aux

faibles valeurs du pH, H^+ remplace les autres cations. Il a été établi que les cations communs se rangent dans l'ordre de facilité de remplacement suivant:

$$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+ \text{ et } Mg^{+2} < Ca^{+2} < Sr^{+2} < Ba^{+2}$$

Les cations bivalents occupent les positions d'échange de préférence aux cations monovalents. Les cations échangeables communs dans la plupart des argiles des sols sont Ca^{+2}.

Les autres phénomènes d'échange discutés sont: échanges d'anions, fixation de cations et d'anions par les argiles, effet du milieu sur les échanges de cations, capacité d'échange des zéolites, des roches, d'autres minéraux, de la matière organique et des complexes organiques, et de la matière minérale amorphe.

Zusammenfassung

Der Ionenaustausch an Tonkomponenten und anderen Mineralen hängt von der Kristallstruktur des Minerals und der chemischen Zusammensetzung derjeningen Lösung ab, die mit dem Mineral in Berührung steht. Die Strukturen der Tonminerale und Zeolithe werden kurz beschrieben, um die Grundlagen zur Diskussion ihrer Ionenaustauschreaktionen zu geben. Ionenaustausch ist in diesen Mineralen ein reversibler chemischer Prozess. Dieser findet statt zwischen Ionen, die von nicht abgesättigten elektrischen Ladungen eines Mineralgitters in der Nähe einer Mineraloberfläche gehalten werden und Ionen in einer Lösung, die in Berührung mit dem Mineral steht. Im allgemeinen ist der Ladungsüberschuss an den Grenzflächen des Minerals negativ und zieht Kationen aus der Lösung an, um diese Restladung abzusättigen. Die chemischen Reaktionen beim Ionenaustausch folgen dem Massenwirkungsgesetz aber sind begrenzt durch die Zahl von Austauschplätzen an der Mineraloberfläche und die Bindungsstärke der austauschbaren Kationen an diese Grenzfläche. Die Titration von Wasserstoff-beladenen Tonen mit Basen zeigt, dass sich Montmorillonite und "Illite" wie ein Gemisch von 2 oder 3 verschiedenen Säuren verhalten. Kaolinit mit seiner nicht definierten Zahl von Austauschplätzen verhalt sich dagegen wie eine nichtdefinierte Zahl von Säuren.

Die Ionenaustausch-Kapazität wird in chemischen Äquivalenten von Basen gemessen, die bei pH 7 gebunden werden. Jedes Tonmineral hat einen Bereich von Austauschkapazitäten wegen der Unterschiede in Struktur und chemischer Zusammensetzung verschiedener Varietaten. Die folgenden Bereiche (in Milliäquivalenten pro 100 g) wurden gefunden: Kaolinit: 3–15, Halloysit ($2H_2O$): 5–10, Halloysit ($4H_2O$): 40–50, Montmorillonit: 70–100, "Illit": 10–40, Vermikulit: 100–150, Glaukonit: 11–20, Attapulgit: 20–30 and allophan 70. Die metallischen Kationen, die gewohnlich in Austauschpositionen in Tonmineralen gefunden werden, sind: Ca^{++}, Mg^{++}, Na^+ und K^+. Bei niedrigen pH-Werten ersetzt H^+ andere Kationen. Die Reihenfolge abnehmender Austauschbarkeit bei häufigen Kationen ist:

$$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+ \text{ und } Mg^{++} > Ca^{++} > Sr^{++} > Ba^{++}.$$

Zweiwertige Kationen gehen bevorzugt gegenuber einwertigen an Austauschplätze. Gewöhnlich tritt als austauschbares Kation in den meisten Tonmineralen der Böden das Ca^{++} auf.

Andere Austauschphänomene werden diskutiert, wie Anionen-Austausch, Fixierung von Kationen und Anionen durch Tonminerale, Austauschkapazität von Zeolithen, von sonstigen Mineralen, von Gesteinen, von organischer Substanz und organischen Komplexen und von amorphen mineralischen Stoffen.

ОЪМЕН ИОНОВ В ГЛИНАХ И ДРУГИХ МИНЕРАЛАХ

Дороти Карролл

Абстракт

Обмен ионов в глинах и других минералах зависит от кристаллической структуры минерала и от химического состава любого раствора находящегося с ними в контакте. Структуры глинистых минералов и зеллитов описаны вкратце для того, чтобы можно было обсуждать их реакции обмена ионов. Обмен ионов в этих минералах представляет собой возвратимую химическую реакцию, которая наблюдается между ионами, удержанными

близко поверхности минерала неуравновешанными электрическими зарядями внутри остова минерала и ионами раствора, находящагося в контакте с минералом. Вообще говоря, избыток заряда на минерале отрицательный; он притягивает катионы из раствора, нейтрализуя этот заряд. Химическия реакции обмена ионов следуют закону действия масс, но реакции ограничены числом мест обмена на минерале, а также силой сцепления взаимнообменяющихся катионов к поверхности минерала. Титрование Н-глин основными реагентами показывает что монтмориллониты (montmorillonites) и "иллиты" ("illites") ведут себя подобно смеси двух или трех различных кислот, в то время как каолинит (kaolinite) имеющий бесконечное количество мест обмена, ведет себя подобно бесконечному числу кислот.

Способность обмена ионов измеряется химическими эквивалентами поглощеннаго основания при pH7. Каждый глинистый минерал имеет свою степень способностей обмена благодаря различию их структуры и химическаго состава. Эти степени /в миллиэквивалентах отнесенных к I00 граммам/ следующие: kaolinite, 3–15; halloysite ($2H_2O$), 5–10; halloysite ($4H_2O$), 40–50; montmorillonite, 70–100; "illite", 10–40; vermiculite, 100–150; glauconite, 11–20; attapulgite, 20–30; and allophane, 70. Обыкновенные металлические катионы, найденные в положениях обмена в глинистых минералах следующие: Ca^{+2}, Mg^{+2}, Na^{+}, and K^{+}. При низких pH числах H заменяет другие катионы. Порядок взаимозамеяемости обыкновенных катионов найден был следующий:

$$Li^{+} < Na^{+} < K^{+} < Rb^{+} < Cs^{+} \text{ and } Mg^{+2} < Ca^{+2} < Sr^{+2} < Ba^{+2}.$$

Двухвалентные катионы вступают в места обмена предпочитательно одновалентным катионом. Обыкновенным взаимозаменяемым катионом в большинстве глинистых минералов в почвах является Ca^{+2}.

Другие рассмотренные явления обмена–обмен анионов, фиксация катионов и анионов глинистыми минералами, влияние среды на обмен катионов, способность к обмену зеолитов, камней, других минералов, органических пород и органических комплексов, и аморфных минеральных материалов.

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Introduction

It is little more than 100 years since the phenomenon of ion exchange was placed on a scientific basis by the work of Thompson (1850) supplemented experimentally by Way (1850), both agricultural chemists. Way's conclusions have formed the basis for most investigations of the cation-exchange capacity of soils (Kelley, 1948, p. 3). Subsequent to the work of Way and Thompson, certain zeolites were found to have properties for exchange similar to

those reported for soils, and it was erroneously believed until about 1930 that zeolitic materials in soils were responsible for ion exchange. It is now known, starting with the investigations of Hendricks and Fry (1930), that the colloid fraction of soils is crystalline, and that ion exchange is associated with the kind and quantity of clay minerals present in soils. Ion-exchange phenomena also occur with other substances, for example the organic matter in soils, minerals, finely crushed rocks, and amorphous materials like silica gel. There are now many publications on cation exchange in soils, clay minerals, and other substances. Selected references are given at the end of this review. The methods used to determine ion-exchange capacity are given by Kelley (1948, p. 74–99) and Jackson (1958, p. 57–109).

Ion exchange, as the term implies, is the exchange of an ion held by a negative charge near a mineral surface with another that is present in a solution in contact with the mineral. The clay minerals and zeolites have noticeable exchange reactions. Broken bonds at the edges of crystalline minerals also allow for ion exchange; the negative charges are accidental in that they are due largely to the particle size of the mineral plates. The adsorption due to these unsatisfied charges can be considered as a part of ion exchange.

Cation exchange in clay minerals can be simply stated thus,

$$\text{Na clay} + \text{H}^+ \rightleftarrows \text{H clay} + \text{Na}^+.$$

However, ion-exchange phenomena are not simple; they vary with the type of clay mineral, nature of replacing ion, pH of solution, concentration in the solution of the replacing ion, the associated ions in the solution, and cations already in the exchange positions of the clay minerals. In the laboratory, and theoretically, certain exchange reactions can be anticipated for simple replacements of ions, but the present state of our knowledge does not allow many such predictions to be made, although exchange reactions are brought about in the application of fertilizers to soils and the conditioning of road-bed materials, two examples among many applications employing cation exchange.

Ion exchange, then, is the reversible process by which cations and anions are interchangeable between mineral surfaces and solutions in contact with the minerals. Physiochemical laws govern the exchanges that can take place in the environment formed by a mineral surface and an electrolyte. Somewhat similar ion exchange may occur between the ions on two mineral surfaces in contact (contact exchange). Ion exchange also takes place between mineral surfaces and root hairs and is an important process in plant nutrition. Cation-exchange capacity is defined as the amount of exchangeable cations, expressed as milliequivalents per gram or per 100 grams of clay (soil or mineral) determined under experimental conditions at pH 7. Figures for cation-exchange capacity are nearly always reported as of this pH, but is is known that, although the exchange capacity is probably a fixed constant for a mineral, different figures would be obtained at different pH values. Because of this, the cation-exchange capacity as determined in the laboratory may not give a true indication of what it actually is under natural conditions in the field.

Many properties of clays are determined by the exchange capacity and the cations in the exchange positions. Rock weathering and soil formation depend largely on the relation of exchangeable cations on mineral surfaces to those in percolating solutions. The exchange capacity and exchangeable cations of clay minerals are important also, for example, in drilling muds, cracking of petroleum, and in various ceramic uses of clays. Ion exchange is the most important process in plant nutrition because ions are exchanged between mineral particles in the soil and root hairs. The determination of the total exchange capacity of a soil, clay, or other mineral is relatively simple and rapid (Kelley, 1948; Jackson, 1958), but the determination of the common exchangeable cations, Ca^{+2}, Mg^{+2}, Na^+, K^+, and H^+, is more complex.

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Clay Minerals and Their Structural Features

General Statement

The clay minerals are micaceous. They are made up of linked silica tetrahedral layers and alumina octahedral layers. The simplest combination, one silica tetrahedral layer with one alumina octahedral layer, is found in kaolinite. It is therefore called a 1:1 layer silicate. Other

clay minerals, montmorillonites for example, consist of two silica tetrahedral layers separated by an alumina layer. Such minerals are called 2:1 layer silicates. The gross structural features of the most important groups of clay minerals are essential background to the discussion of cation exchange processes, and these as revealed by X-ray examination, are described below.

Fundamental also to an understanding of ion-exchange phenomena is the fact that the silicate structures are determined by the ratios of the positive to the negative ions (Hendricks, 1945, p. 626), the ratios of the ionic radii which determine the co-ordination figures for the positive ions, and a general "principle of microscopic neutrality," as first recognized by Pauling (1930). Cations at exchange positions conform to the requirements of microscopic neutrality in that they are opposite negatively charged positions in the crystal structure.

Kaolinite Group

The kaolinite unit is formed by the combination of one tetrahedral and one octahedral layer. The atomic planes in kaolinite are

		Charges	
Si-tetrahedron	$6\ O^{-2}$	-12	
	$4\ Si^{+4}$	$+16$	
Al-octahedron	$4\ O^{-2} + 2(OH)^-$	-10	-28
	$4\ Al^{+3}$	$+12$	$+28$
	$6\ (OH)^-$	-6	

Kaolinite sheets are neutral. One surface is terminated by $(OH)^-$ ions, and the opposite one by O^{-2} ions. The sheets are held firmly together by the hydrogen bonding of the $(OH)^-$ ions on the bottom of one layer to O^{-2} ions on the top of the neighboring layer (Hendricks, 1945, p. 629). Kaolinite attracts external cations only by negative charges of terminal O^{-2} ions exposed on the edges of the structural sheets. Because of this, grain size affects the cation-exchange capacity.

The halloysite-type clay minerals have the same structure as kaolinite. There are two forms of halloysite, one of which contains a layer of water between the kaolinite layer units that increases the basal spacing from 7.2 to 10.1 Å. This is the $4H_2O$ form or endellite, and it has a much higher exchange capacity than the $2H_2O$ form (halloysite or metahalloysite). Electronmicrographs show that the $4H_2O$ form consists of tubes made up of overlapping curved sheets of kaolinite type. On dehydration to the $2H_2O$ form the tubes frequently collapse, split, or unroll. The curvature can develop, according to Grim (1953, p. 55), because of the irregular stacking of the layers and the interlayer water molecules which cause a weak bond between successive layers. The ion-exchange capacity of halloysite is greater than for kaolinite and has a wider range, but more data are required to characterize this range adequately. One difficulty is the dehydration that takes place when halloysite samples are kept in the laboratory. The exchange capacity is given in Table 1.

Micaceous Clay Minerals

The mica unit is formed by the combination of one octahedral layer between two tetrahedral layers. Minerals with this structure are the micas, hydrous micas ("illites"), montmorillonite group, vermiculites, glauconites, and celadonites. The tetrahedral and octahedral sheets are combined so that the tips of the tetrahedra of each silica sheet and one of the hydroxyl layers of the octahedral sheet form a common layer. The atoms common to both the tetrahedral and octahedral layers become O^{-2} instead of OH^-. The layers are stacked one above the other in the c direction; thus, O^{-2} layers of each unit are adjacent to O^{-2} layers of the neighboring units with the consequence that there is a very weak bond and an excellent cleavage between the layers.

There are two types of mica, the dioctahedral and the trioctahedral. In the dioctahedral micas only two-thirds of the octahedral positions are occupied, and the charge is principally in the tetrahedral layer, but it varies in different members of the group until in the mineral celadonite the charge is almost wholly octahedral. In the trioctahedral micas all the octahedral positions are occupied by divalent cations. Substitution of these divalent cations by trivalent cations produces either a positive charge on the octahedral layer or a decrease in the number of octahedral positions occupied, or both. The negative charge is on the tetrahedral layers and must be great enough to neutralize the positive octahedral charges and still give the structural unit a negative charge of approximately 1.0. The dioctahedral type of mica is found in muscovite, "illites," glauco-

nite, and celadonite. The trioctahedral type of mica is found in biotite and vermiculite.

Brindley and MacEwan (1953) consider that there are no sharp lines of demarcation between the micas proper, the hydrous micas (a broad term covering "illites" and mixed-layer minerals), and the montmorillonites and vermiculites. However, Yoder and Eugster (1955) have shown that most minerals that have been called hydrous micas, "illites," hydromica, and hydromuscovite are mixed-layer structures.

The following is the arrangement of atomic planes in muscovite, a dioctahedral mica:

		Charges	
	Interlayer K^+	$+1$	
Si-tetrahedron	$6\ O^{-2}$	-12	
	$3\ Si^{+4}, 1\ Al^{+3}$	$+15$	
Al-octahedron	$4\ O^{-2}, 2(OH, F)^-$	-10	-44
	$4\ Al^{+3}$	$+12$	$+42$
	$4\ O^{-2}, 2(OH, F)^-$	-10	
Si-tetrahedron	$3\ Si^{+4}, 1\ Al^{+3}$	$+15$	
	$6\ O^{-2}$	-12	
	Interlayer K^+	$+1$	

The excess of negative charge is neutralized by K^+ ions between adjacent layers, thus binding them together. The bond is strong enough to prevent the entry of water molecules between the layers, and the mineral does not expand. Deficiency in K^+ leaves the structural unit with a negative charge that is neutralized by exchange cations. Similarly the addition of K^+ stabilizes the structure by neutralizing the negative charges. Theoretically, isomorphous replacements can and do take place in both the silica tetrahedra and the alumina octahedra. The small exchange capacity of muscovite is due to the fact that the negative charge on the structural unit is neutralized by K^+, and no exchangeable cations are present.

The "illite" clay minerals, or hydrous micas, differ, according to Grim (1953, p. 67), from muscovite in several ways. There is less substitution of Al^{+3} for Si^{+4}. In well-crystallized micas one-fourth of the Si^{+4} is replaced, whereas in the "illites" about one-sixth is replaced. As a consequence of this lesser substitution, the silica to alumina tetrahedral ratio is higher, and the net unbalanced charge deficiency is reduced from 2 per unit cell to about 1.3 per unit cell. Even so, the K^+ ions between the unit layers are not sufficient to neutralize all the charge, and other cations—Ca^{+2}, Mg^{+2}, and H^+—are also present. There is some randomness in the stacking of the layers in the c direction, and the size of the "illite" particles is very small—1–2 microns or less. Yoder and Eugster (1955, p. 249) report that the Fithian "illite" is a mixed-layer 1 Md + montmorillonite and 2 M (Md = randomly stacked one-layer monoclinic; 2M = two-layer monoclinic muscovite). The cation-exchange capacity ranges from 10 to 40 milliequivalents per 100 gram.

Glauconite is an important micaceous mineral that has the structure of a dioctahedral mica. It occurs in great abundance in certain sedimentary rocks of marine origin—for ex-

TABLE 1— CATION-EXCHANGE CAPACITY OF CLAY MINERALS

Mineral	Structural control	Exchange capacity, m.e./100 g at pH 7
Kaolinite	Unsatisfied valences on edges of structural units	3–15
Halloysite ($2H_2O$)	Unsatisfied valences on edges of structural units	5–10
Halloysite ($4H_2O$)	Unsatisfied valences on edges of structural units and on internal surface between the layers	40–50
Montmorillonite group	Substitutions in the octahedral and tetrahedral units giving excess negative charge; unsatisfied valences on edges of units.	70–100*
"Illites" (hydrous micas)	As in montmorillonite, plus deficiency of K^+ between the layers	10–40
Vermiculite	Replacement of interlayer cations, substitution within the units, and unsatisfied valences on edges of units	100–150
Chlorite	No data. Possible deficiency of charge due to substitution in the brucite layer	10–40?
Glauconite	As in "illites"	11–20+
Palygorskite group	Substitution of Al^{+3} for Si^{+4} in structural units, unsatisfied exchange sites within channels in the structure	20–30
Allophane	Porous amorphous structure with unsatisfied valences	~70

* Certain members of the montmorillonite group have a much lower exchange capacity because there is no substitution in the tetrahedral or octahedral units—for example, stevensite with 36 meq./100 g.

ample, the Navesink and Hornerstown formations of New Jersey. Glauconite is of interest because it is probably the first clay mineral in which the exchange capacity was investigated and made use of commercially, namely for water softening. The exchange capacity is caused by considerable replacement of Al^{+3} by Fe^{+3}, Fe^{+2}, and Mg^{+2}. There are charge deficiencies in both tetrahedral and octahedral layers. The interlayer cation, K^+, is deficient, but Ca^{+2} and Na^+ are present as exchangeable cations to neutralize the structure as a whole. Glauconite and celadonite have been described by Hendricks and Ross (1941) who give the average formula for glauconite as:

$$(K, Ca_{1/2}, Na)_{0.84}(Al_{0.47}Fe_{0.97}^{+3}Fe_{0.19}^{+2}Mg_{0.40}^{+2})(Si_{3.65}, Al_{0.35})O_{10}(OH)_2$$

The interlayer cation content is definitely less than one equivalent. Glauconite varies in its chemical composition and in its physical appearance. X-ray examination shows that it is structurally often interlayered with "illite," and exchange capacities are sometimes high enough to suggest that it may also be interlayered with montmorillonite. Glauconite has an ion-exchange capacity in the range of the hydrous micas, 10 to 40 milliequivalents per 100 gram. An average figure quoted for its use as a water softener is 30 grains of $CaCO_3$ removed per pound of greensand (glauconite screened to a certain size). This is approximately equal to 20 milliequivalents Ca^{+2} per 100 gram. The exchange capacity of glauconite is increased by heating, or treatment with NaOH, or both. Treatment with NaOH results in a partial decomposition, as in halloysite, with consequent increase in surface area and therefore increase in exchange capacity due to broken bonds at the edges and surfaces of the grains. The effect of heating may be only physical—that is, strengthening the individual grains against breakdown during use.

As glauconite occurs in large quantities it provides useful research material for investigating the exchange properties of the micaceous clay minerals. Glauconite can be separated from other minerals found with it, graded as to grain size, and examined by X-ray diffraction. The exchangeable cations can therefore be related to the composition and structure.

Celadonite is very similar to glauconite, but it is formed as an alteration product of olivine in basalts. It is assumed that it has a range in ion-exchange capacity similar to glauconite. The presence of celadonite in basalt would tend to increase the over-all exchange capacity of such rocks, as, for example, in the Snake River basalt. In some instances montmorillonite is also an alteration product of olivine.

Montmorillonite Group

The original montmorillonite is a clay from Montmorillon, France, described by Damour and Salvetat (1847). The montmorillonite group of minerals was established by Ross and Hendricks (1945) as a result of their systematic description of clay minerals similar in structural features to the original montmorillonite. The members of this group, however, vary widely in chemical composition. The term "montmorillonoid" was introduced by MacEwan (1951) to replace the use of "member of the montmorillonite group" as given by Ross and Hendricks. Subsequently minerals of this group have been called "montmorins" by Correns (1951) and smectites by the British clay mineralogists (Brown, 1955, p. 296). Smectite actually has priority over montmorillonite as a mineral name, but it had not been used for many years before its suggested revival.

The montmorillonite structure is the same as that of mica, but the layers are not held together by K^+ ions, and water and other polar molecules, such as organic molecules, can enter between the unit layers and cause expansion. Exchangeable cations occur between the structural units where they are loosely held by excess negative charges within the units. The c-axis spacing of completely dehydrated montmorillonite depends on the size of the interlayer cation, and the thickness of the water layers between the silicate units also depends on the kind of exchangeable cation present at any given water-vapor pressure.

The theoretical charge distribution, without considering substitutions within the layers, is as follows:

		Charges	
Si-tetrahedron	$6\ O^{-2}$	-12	$+44$
	$4\ Si^{+4}$	$+16$	
			Layer common to tetrahedral or octahedral sheets
Al-octahedron	$4\ O^{-2}2(OH)^-$	-10	
	$4\ Al^{+3}$	$+12$	
			Layer common to tetrahedral or octahedral sheets
	$4\ O^{-2}2(OH)^-$	-10	
Si-tetrahedron	$4\ Si^{+4}$	$+16$	-44
	$6\ O^{-2}$	-12	

The investigations of Ross and Hendricks (1945) and of Foster (1951) have done much to explain the exchange relations in montmorillonite. The general formula for members of the montmorillonite group is

	Ions in octahedral co-ordination	Ions in tetrahedral co-ordination	
Sheet	↓		$O_{10}(OH)_2$

Exchange cations external to sheet held because of a deficit in the positive charge in octahedral or tetrahedral positions.

The structural formula of a montmorillonite from Belle Fourche, South Dakota (Foster, 1951, p. 724), is

$$[Al_{1.47}{}^{+3}Fe_{.18}{}^{+3}Fe_{.02}{}^{+2}Mg_{.23}{}^{+2}]$$

$$[Si_{3.91}{}^{+4}Al_{.09}{}^{+3}]O_{10}[OH]_{2x.35}.$$

Ross and Hendricks (1945) stressed the importance of substitution in the montmorillonite structure. For every 12 oxygen-hydroxyl ions, there are 4 tetrahedral positions that must be filled with Si^{+4} ions, which can, however, be partly replaced by Al^{+3} ions. Correspondingly there are 3 positions having octahedral co-ordination of which 2 to 3 may be occupied by Al^{+3}, Fe^{+3}, Fe^{+2}, Mg^{+2}, Mn^{+2}, Zn^{+2}, Co^{+2}, Cu^{+2}, Cr^{+3}, or Li^{+}. Substitution of Al^{+3} for Si^{+4} in the tetrahedral unit, or of bivalent ions for Al^{+3} in the octahedral unit, results in an electrically unbalanced structure with an excess negative charge. Analyses of minerals of the montmorillonite group show that the exchangeable ions are restricted to one-third of an equivalent per $O_{10}(OH)_2$ unit (Hendricks, 1945, p. 627–628). The exchangeable cations are held between the unit layers and around their edges. Distance from the source of the charge deficiency is important in determining the strength of the bonding of the exchangeable cation to the layers. The principal cations held in the exchange positions are Ca^{+2}, Mg^{+2}, Na^{+}, K^{+}, and H^{+}. There is generally very little exchangeable K^{+}, probably because its ionic radius is 1.33 Å and is rather large when compared with 0.66 Å for Mg^{+2} which is readily exchangeable. Foster (1951) first showed the importance of exchangeable Mg^{+2} and recalculated some of the analyses by Ross and Hendricks (1945) to obtain better structural formulas. Removal of impurities such as free silica and free alumina (Foster, 1953) also gives more accurate figures for the cations in the tetrahedral unit of montmorillonite.

Most montmorillonites have an exchange capacity of 70 to over 100 milliequivalents per 100 grams but stevensite as reported by Faust and Murata (1953) has an exchange capacity of only about 36 milliequivalents per 100 grams. This is explained by the lack of substitution in the tetrahedral unit. The following structural formulas illustrate the relation of the charge deficiency to the octahedral and tetrahedral units in stevensite, hectorite, and saponite (Faust and Murata, 1953, p. 982).

$$\text{Stevensite (New Jersey)} \quad \overset{(Ca/2,\,Mg/2)_{.15}}{\uparrow}\ (Mg_{2.88}Mn_{.02}Fe^{+3}_{.02})(Si_4)O_{10}(OH)_2$$

$$\text{Hectorite (California)} \quad \overset{Na_{.33}}{\uparrow}\ (Mg_{2.67}Li_{.33})(Si_4)O_{10}(OH)_2$$

$$\text{Saponite} \quad \overset{(Mg/2)_{.38}}{\uparrow}\ (Mg_{2.93}Fe^{+2}_{.05}Fe^{+3}_{.02})(Si_{3.68}Al_{.32})O_{10}(OH)_2$$

Vermiculite

The vermiculite structure consists of sheets of trioctahedral mica or talc separated by layers of water molecules occupying a definite space (4.98 Å) which is about the thickness of two water molecules. The structure is unbalanced chiefly in substitutions of Al^{+3} for Si^{+4} which may be partly balanced by other substitutions within the mica lattice; there is always a residual net-charge deficiency of 1 to 1.4 per unit cell. This charge deficiency is satisfied by cations that occur between the mica layers and are largely exchangeable. The exchange capacity is of the same order as in montmorillonite, and may be higher. The balancing cation is Mg^{+2}, sometimes with Ca^{+2} also present. The following is the arrangement of the structural units in vermiculite.

yH_2O double water layers

		Charge
Si-tetrahedron	$x(Mg^{+2}\ Ca^{+2})$	$+x$
	$6\ O^{-2}$	-12
	$(4-x)Si^{+4}\cdot xAl^{+3}$	$+(16-x)$
Al-octahedron	$4\ O^{-2}\ 2(OH)^{-}$	-10
	$6(Mg\ Fe)^{+2}$	$+12$
	$4\ O^{-2}\ 2(OH)^{-}$	-10

Si-tetrahedron	$(4 - x)Si^{+4} \cdot xAl^{+3}$	$+(16 - x)$
	$6\ O^{-2}$	-12
	$x(Mg^{+2}\ Ca^{+2})$	$+x$
	yH_2O double water layers	
	$x = 1$ to 1. 4	
	$y =$ about 8	

The nature of the exchangeable cations influences the size of the interlayer water as these cations occur between the mica layers. Walker (1951) gives the thickness of the water layer in vermiculites as follows:

Cation	*d* (002) *Å*	*Thickness of water layer, Å*
Mg^{+2}	14.39	5.11
Ca^{+2}	15.0	5.75
Ba^{+2}	12.3	3.04
Li^{+}	12.2	2.94
Na^{+}	14.8	5.55
K^{+}	10.6 (diffuse)	1.34 (approximate)
NH_4^{+}	10.8 (diffuse)	1.54 (approximate)

The water exists in two forms, bound and unbound. The bound water occurs around the Mg^{+2} ion as a hydration envelope of 6 water molecules for each Mg^{+2}. The unbound water fills the space between the octahedral groups of water. The ratio of unbound water to total interlayer water is about 8 to 14. Vermiculite differs from montmorillonite in that the expansion with water is limited to about 4.98 Å. Vermiculites adsorb certain organic molecules between the mica layers but differ from montmorillonite in that the adsorbed layer is thinner and less variable.

Chlorite

The structure of chlorite consists of alternate micalike and brucitelike layers. The micalike layers are trioctahedral with the general composition $(OH)_4(SiAl)_8(Mg, Fe)_6O_{20}$, and the brucitelike layers are $(Mg, Al)_6(OH)_{12}$. The mica layer is unbalanced by substitution of Al^{+3} for Si^{+4}, and this deficiency of charge is balanced by an excess charge in the brucite sheet as a consequence of substitution of Al^{+3} for Mg^{+2}. The charge distribution is as follows, where $x = 1$ or 2:

	Charges
Brucite layer	
$6\ OH^{-}$	-6
$(6 - 2x)Mg^{+2}\ 2xAl^{+3}$	$+[2(6 - 2x) + 3(2x)]$
$6\ OH^{-}$	-6
Mica layer	
$6\ O^{-2}$	-12
$(4 - x)Si^{+4}\ xAl^{+3}$	$+ [4(4 - x) + 3x]$
$4\ O^{-2}\ 2(OH)^{-2}$	-10
6 R (Trioctahedral, R = Mg^{+2}, Mn^{+2}, Fe^{+2}, Fe^{+3}, Cr^{+3}, Ti^{+4})	$+12$
$4\ O^{-2}\ 2(OH)^{-2}$	-10
$(4 - x)Si^{+4}\ xAl^{+3}$	$+ [4(4 - x) + 3x]$
$6\ O^{-2}$	-12

The above data are for the chlorite group of minerals, members of which occur in rocks. Fine-grained chlorites have been identified in soils, but it has not been possible to isolate samples for cation-exchange studies. As with other members of the chlorite group and of the mica group, isomorphous replacement gives a variety of different chlorites. Soil chlorites may differ from well-crystallized material in having a somewhat random stacking of the layers, and in hydration.

Mixed-Layer Minerals

Many micaceous clay minerals consist of layers of two different minerals. The mixed-layer structure may be either random or regular interstratification. The most usual occurrence has layers with two different degrees of hydration—for example, a mixture of mica-type layers with montmorillonite or vermiculite-type layers. Interstratification of montmorillonite and halloysite may also occur. The chemical composition and cation-exchange capacity are variable in these minerals. Mixed-layer minerals are common in soils. Yoder and Eugster (1955, p. 249–256) discuss the micaceous clay minerals and give data on the composition of many specimens from different localities. The Fithian "illite" is a mixed-layer mineral consisting of layers of 1 Md (one layer monoclinic) plus montmorillonite and 2 M (two-layer monoclinic) muscovite.

Palygorskite (Attapulgite) Group

In the sepiolite-palygorskite-attapulgite group, the structually important element is the amphibole-type double silica chain with its long direction parallel to the c axis. Bradley (1940) described the structure of attapulgite. Marshall and Caldwell (1947) discussed the cation-exchange capacity and the relation to the water channels. There is much "zeolitic water"—that is, loosely held in the lattice and

lost at low temperatures. Chains of water molecules running parallel to the c axis fill the interstices between the amphibole chains. The cation-exchange capacity of attapulgite is about 20 milliequivalents per 100 gram.

Allophane

Allophane is generally considered to consist of random arrangements of silicon in tetrahedral co-ordination and aluminum (plus metallic cations) in octahedral co-ordination. The randomness of structure causes most allophane to be amorphous to X rays, but some more highly organized allophane has also been reported (White, 1953). The cation-exchange capacity is due to unsatisfied bonds caused by the disordered structure and may be as high as 70 milliequivalents per 100 gram.

Cation-Exchange Capacity of Clay Minerals and Soils

General Discussion

The exchange capacity of the various clay minerals is given in Table 1 (Grim, 1953, p. 129, with modifications).

Variation in exchange capacity for the individual minerals is caused by differences in availability of exchange sites—that is, position of negatively charged spots on the particles—and by the chemical composition that causes the negative charges to develop. Irregularities in the lattice structure and variation in grain size increase the ion-exchange capacity by providing a greater number of unsatisfied bonds at the edges. This is particularly noticeable in kaolinite and halloysite. The exchange capacity increases as the grain size of a clay mineral *decreases* because there is a larger surface area and more broken bonds. Hendricks (1945) has shown that the exchange capacity of kaolinite increases from about 2 milliequivalents per 100 gram with a specific surface area of 10 square meters per gram, to 8 milliequivalents per 100 gram with a specific surface area of 40 square meters per gram. Reduction in grain size together with disordered lattice structure tends to produce a mineral amorphous to X rays. Such minerals have higher exchange capacities than larger, better crystallized grains of similar composition because of increased surface area and more broken bonds. Materials like silica gel have exchange capacities in the range of 70 to 100 milliequivalents per 100 gram. However, such exchange is related more to adsorption than to true cation exchange.

In the inorganic part of most soils, the figures obtained for cation exchange are those produced by mixtures of clay minerals. An attempt has been made (Hathaway and Carroll, 1954) to characterize such clays from X-ray diffraction data. The exchange capacity of soils depends on a number of factors:

(1) Quantity of clay and silt fractions. The silt fractions generally have an appreciable exchange capacity.

(2) The kind of clay mineral present—for example, a small quantity of montmorillonite, vermiculite, or "illite"—will give a greater exchange capacity than a very much larger amount of kaolinite.

(3) The amount of organic matter present. Much organic matter increases the exchange capacity irrespective of the clay minerals present.

(4) Ion-exchange capacity figures for the clay fractions are only a slight indication of the clay minerals present when mixtures of clay minerals occur. Because of this, the exchange-capacity figure should not be used as the only indication of the presence of certain clay minerals. The data should be supplemented by X-ray diffraction study.

Mechanics of Cation Exchange

Ion exchange takes place when a solution containing cations and anions comes in contact with a mineral surface. The reactions are due to the structure and chemical composition of the mineral and to the chemical elements in the solution in contact with the mineral. It is not possible to describe the effects due to the mineral structure without also considering the contact solution, and vice versa.

Following the work of Hendricks (1945), Brindley and MacEwan (1953) summarized the structural causes for cation exchange in the clay minerals thus,

(1) Unsatisfied valences produced by "broken bonds" at surfaces and edges of particles

(2) Unbalanced charges caused by isomorphous substitution of cations—for example, Al^{+3} substituted for Si^{+4}

(3) Dissociation of structural OH^- radicals the H^+ of which may be replaced by metallic cations

(4) Accessibility of structural cations other than H^+ which become exchangeable under certain conditions—for example, at low pH

values Al^{+3} ions move from the octahedral units to the exchange positions.

The principal cause of cation exchange in montmorillonites, "illites," and vermiculites is isomorphous replacement. "Broken bonds" are the most important cause of cation exchange in kaolinite, halloysite, and in fine particles of other minerals such as quartz.

Hendricks (1945, p. 626) tabulated the cations that are important in exchange reactions as follows:

Type of co-ordination position	Number of oxygen neighbors	Important cation	Ionic radius for observed co-ordination with oxygen
Tetrahedral	4	Si^{+4}, Al^{+3}	0.55 Å
Octahedral	6	Al^{+3}, Mg^{+2}, Fe^{+3}, Fe^{+2}, Li^{+}	0.55 to 0.80 Å
Greater than octahedral	>6	K^{+}, Na^{+}, Ca^{+2}, Ba^{+2}	0.95 Å

The micelles of clay minerals present a number of charged spots that attract cations and anions in a solution surrounding the micelles. Ion exchange is thus, in part at least, a surface phenomenon, as even the interlayer cations can be considered as part of an extended surface. The fact that there are different positions on the clay micelles, which are themselves electrically charged colloidal particles, for the negative charges causes replacement to take place at different levels. Thus, in montmorillonite, exchange takes place at three sites: on the flat surfaces, on the edges, and between the silica and alumina layers where ions are loosely held to neutralize deficiencies in these layers caused by isomorphous replacements (Ross and Hendricks, 1945). The excess negative charge on the mineral is neutralized by an equivalent amount of positive ions. In natural situations the most common exchangeable cations are Ca^{+2}, Mg^{+2}, H^{+}, Na^{+}, and K^{+}. Calcium is the dominant cation in soil clay minerals.

Ion exchange takes place in a water film that surrounds a micelle of clay or a mineral grain. This water film is considered to be a diffuse double layer as described by Verwey and Overbeek (1948). The double layer is a space containing water and an ion swarm that is dependent on the surface-charge density of the mineral surface (the surface of the clay micelle), the kinds of exchangeable cations, the concentration of electrolytes in the solution, and, to a lesser degree, on the temperature. The charge density of the clay-mineral surface depends on the kind of mineral and on the cations (and anions) already present. According to Wiklander (1955, p. 110)

> "The exchangeable ions are surrounded by water molecules and may thus be considered as forming a solution which is often called the *micellar solution* or *inner solution* in distinction to the outer solution of free electrolytes, the so-called *inter-micellar* or *outer solution*."

The exchangeable cations are held to the mineral surface by coulomb forces.[1] Hendricks (1941) has shown that van der Waals forces[2] are also involved in the adsorption of organic cations by montmorillonite. Recently Emerson (1957) has shown that

> "The space occupied by the organic molecules is determined by subtracting the van der Waals thickness of individual clay sheets from the observed (001) spacing, and is normally less than that calculated by assuming that the molecules lie as flat as possible and also make van der Waals contact with the surface atoms of the clay."

There are a number of theories of the distribution of positive and negative ions in the double layer. Verwey and Overbeek (1948) consider that the diffuse double layer at a plane surface (the surface of the mineral) has a negative charge. The concentration of the exchangeable ions is highest in the immediate vicinity of the surface and decreases toward the intermicellar surface of uniform composition. The double layer contains ions with negative as well as positive charges that come from the free electrolyte (the solution in contact with the mineral). The charge density of the particle surface, σ, is equal to the sum of charges in the inner layer, σ_1, and in the outer layer, σ_2, or

$$\sigma = \sigma_1 - \int_0^\infty \rho d\,(x - \delta)$$

ρ = space net charge density, x = distance from the surface, and δ = thickness of inner layer of ions (depending on the volume of adsorbed ions present in a monolayer).

However, clay micelles cannot be considered as simple plane surfaces because there are spots at which negative charges occur, so that the Gouy theory (Wiklander, 1955, p.

[1] Electrostatic forces between charged particles.
[2] Weak forces that cause packing together of atoms and molecules.

111) would apply only if the surface of the clay micelles were made extremely small. It has been shown that the clay minerals vary, because of their structure, in the amount of inherent and accidental charges. Marshall (1949, p. 20–22) has pointed out that particle size, porous structure, and charged framework are all important features of ion exchange. Minerals with a charged framework, such as montmorillonite, have a high exchange capacity because of substitutions within the tetrahedral and octahedral layers producing a strong negative charge that holds exchangeable cations between the structural units. Kaolinite has a simple chemical composition with little or no substitution in the units, and the charge is solely due to unsatisfied valences at the edges of the micelles. The number of such broken bonds depends on the particle size; thus a kaolinite separated from a soil was found to have a surface area of 80 square meters per gram. With an exchange of 0.12 milliequivalents per gram there is an area of about 20 square Angstroms for each univalent cation (Nelson and Hendricks, 1943). It seems, therefore, that the Donnan equilibrium describing the state of equilibrium of a system containing a membrane impermeable to one ion species more accurately pictures the mechanism of ion exchange than does the Gouy-Stern theory (Wiklander, 1955, p. 111, 116). For a system containing the nondiffusible electrolyte RM and the diffusible electrolyte MA, Donnan showed that the following relation holds: $(M^+)_i(A^-)_i = (M^+)_o(A^-)_o$, when $(M^+)_i$ and $(M^+)_o$ represent the activity of the inside and outside solutions of the cation M^+.

The relation between the clay micelle surfaces and the composition of a solution in contact with these surfaces has been studied by Mattson and Wiklander (1940), Ganguly and Mukherjee (1951), Marshall (1954), Wiklander (1955), Mitra (1942), and others. A clay mineral in the hydrogen form has all the exchangeable cations originally present replaced by H^+ ions and will therefore react with bases in a manner similar to the reaction of an acid with a base. However, the H^+ ions are attached to the clay micelle and do not become completely dissociated in water or other liquids. If an H clay is titrated with a base such as NaOH, the pH of the clay suspension is raised, and a titration curve of pH against concentration of base may be drawn. There are several complicating factors: H clays nearly always have Al^{+3} present in an exchangeable form, the clay salts are only partly ionized in solution, the H^+ ion is more strongly held in certain positions on the mineral lattice than on others (Garrels and Christ, 1956), and at high and low pH values there is partial decomposition of the clay mineral giving rise to aluminates and silicates in solution. Some silica is soluble at all pH values, but alumina is soluble only below pH 4 and above pH 9. The clay minerals vary in their reactions with bases according to their structure. Kaolinite reacts like a number of simple acids because the exchangeable cations are held on the edges of the micelles where broken bonds occur. All the exchange sites are apparently of equal value. In the more complex clay minerals the exchange sites are not of equal value (equal charge intensity), and the reactions are similar to the titration of two or three mixed acids with a base.

In titration curves for various H-clay minerals with a base it is usual to find slopes of different steepness after different quantities of base have been added. The curves represent ionization of the base added—for example, Na^+ is adsorbed liberating OH^- which changes the pH values. If there is no ionization, the slope flattens and is often a straight line for the addition of several increments of base. The energy relationships in cation exchange have been summarized by Marshall (1950, p. 73). The ionic activity coefficient of a true solution depends on the ionic strength μ of the solution, and $\mu = \frac{1}{2}\sum c_i z_i^2$ where c_i = molarity of the ionic species i whose valency is z_i. In clay systems the term fraction active (f) is analogous to the activity coefficients of ions in true solution. The mean free-bonding energy of a given cation is

$(\Delta F)_{\text{cation}} = RT \ln \frac{c}{a_1}$, where a_1 is the measured activity and c that which would be given for complete ionization—that is, the total concentration of the cation. Since the fraction active $f = \frac{a_1}{c}$ then $(\Delta F)_{\text{cation}} = RT \ln \frac{1}{f}$.

Four rules for ionization for surfaces have been formulated by Marshall (1954) from the results of numerous experiments with clay minerals:

(1) If the bonding energy per exchange site

on the mineral remains the same while the cation present in a solution changes, then the fraction active (f) for a polyvalent cation of valency n is obtained by taking that of the univalent cation to the power n. Considerable differences are found in the fractions active among both univalent and polyvalent cations. With univalent cations the normal hydration series is followed. Sodium has a lower bonding energy than potassium because the Na^+ ion has a greater hydration. Among bivalent cations, however, there are different orders of bonding energy for the same cations with the various clay minerals. Thus kaolinite has the order Mg > Ca > Ba, and "illite", Ba > Ca > Mg. Fixation (to be discussed later) of certain cations probably plays an important role in the relationship between the bonding energy and the different cations adsorbed by clay minerals. Complete dissociation of a cation from a silicate surface corresponds to $f = 1$ and $(\Delta F)_{\text{cation}} = 0$.

(2) Dissimilar ionizing surfaces show increasingly greater disparity as the valency of the cation increases. Marshall (1954, p. 370) explains this rule by considering two monofunctional surfaces with bonding energy $(\Delta F)_1$ and $(\Delta F)_2$ corresponding to fractions active f_1 and f_2 for monovalent cations. With a cation of valency n the bonding energies will be $n(\Delta F)_1$ and $n(\Delta F)_2$, and the respective fractions active $(f_1)^n$ and $(f_2)^n$. The ionization ratio which was f_1/f_2 for monovalent cations thus becomes $(f_1/f_2)^n$ for the polyvalent. Curves showing the mean free bonding energy indicate considerable differences between Ca montmorillonite and Ca attapulgite, but the differences between K montmorillonite and K attapulgite are not nearly so great. The structure of these two minerals is different, and this results in differences in the position and charge of the surfaces that can adsorb cations.

(3) The monovalent cation/divalent cation activity ratios for dissimilar surfaces should fall in the inverse order of the fractions active for monovalent cations if comparisons are made at the same relative cation concentration. This rule shows to best advantage when the activity ratios are calculated for clays fully saturated with potassium or calcium. The following figures (Marshall, 1954, p. 374) illustrate this rule:

	Equivalence m.e./100 g.	Cation conc. m.e./100 g.	f_K	a_{Ca}/a_K
Kaolinite	2.75	2.75	0.309	0.220
Attapulgite	30	4.5	0.289	0.169
Bentonite (Wyo.)	100	5.0	0.202	0.140
Illite (Maquoketa)	22.5	11.25	0.155	0.150
Illite (Grundite*)	28.5	13.75	0.145	0.087
Beidellite (Putnam)	70	17.50	0.118	0.057
Bentonite (Ariz.)	120	18.0	0.079	0.049

f_K = fraction active for potassium; a_{Ca}/a_K = activity ratio.

* A bonding clay produced by Illinois Clay Products Co., an underclay of Pennsylvanian age; it consists of 70 per cent illite with kaolinite and impurities.

(4) In multifunctional systems containing more than one cation, the sum of the mean free bonding energies are at a maximum. The cation with the highest free bonding energy preempts those positions on the surface having the higher bonding energy, leaving the cation with the lowest free bonding energy to take the positions with lower free bonding energy. This is known as Jarusov's rule (1937). Thus, one cation affects the bonding energy and activity of another through the energy relationships of the ionizing sites on the surface and those in the ionic atmosphere (solution in contact with the mineral surface). The application of this rule favors the bonding of bivalent cations to clay minerals with a strong negative charge—that is, many sites of negative charge and therefore a high cation-exchange capacity.

The interpretation of these four rules together with a consideration of the reactions that take place according to the law of mass action serves to explain many of the exchange reactions found by experiment. Cation-exchange reactions in natural situations are more complex because the concentration of cations and anions in waters percolating through rocks and soils is seldom known, nor are the initial reactions of the silicate minerals in releasing cations by exchange or by solution.

The reversible exchange reactions between cations in an electrolyte and those held in the exchange sites of clay minerals are chemical reactions. Attempts have been made to express the results of such reactions as equations. The clay minerals are chemical compounds

that can become dissociated only to a limited extent through their exchangeable cations that are held by different bonding energies to different exchange sites on the minerals. Any equations expressing exchange reactions have to take into account the different bonding energies and the different kinds of exchange sites. No such equations have so far been formulated, but the investigations in this field have been summarized by Kelley (1948, p. 40–50) and Wiklander (1955, p. 114–127).

There are two principal kinds of equations that have been used to express cation-exchange reactions. The first kind of equation, based on Freundlich's adsorption isotherm originally derived from the adsorption of a gas by a solid, is $\frac{x}{m} = kp^{1/n}$. As applied to cation exchange, x/m = amount of cations taken up from a solution at equilibrium with a given weight of mineral, p = amount of added cation remaining in solution, k and n are constants. Langmuir (1918), Wiegner and Jenny (1927), and Vageler (1930) published modifications of Freundlich's equation. Kelley (1948, p. 41–42) points out that the constants of the equations have no particular meaning in terms of the properties of the clay.

The second kind of equation proposed to explain cation-exchange reactions is based on the law of mass action which formulates the idea that in a chemical reaction such as A + B $\rightleftarrows$ C + D, in general, or in clay minerals, Na^+ + H clay $\rightleftarrows$ H^+ + Na clay, in particular, an equilibrium is attained. The law of mass action operates in any chemical reaction. In clays and soils it can be applied only if the ions in solution and those in exchange positions on the clay minerals can be determined quantitatively. Furthermore, the law of mass action is theoretically applicable to the reactions that take place in the diffuse double layer of solution in contact with clay minerals and to the state of equilibrium existing in a system containing a membrane impermeable to one-ion species—that is, the Donnan equilibrium.

Soils and not clay minerals were used in the early experimental work on exchange reactions because the results were needed to determine fertilizer requirements, and because it was not at first known that the clay minerals are largely responsible for the exchange capacities of soils. Kerr (1928a, 1928b) was one of the first to apply the mass-action equation to exchange reactions in soils. The equations that he gave for reactions with univalent and bivalent cations are

$$\text{K soil} + Na^+ \rightleftarrows \text{Na soil} + K^+,$$

$$\text{and} \quad \text{Ca soil} + 2K^+ \rightleftarrows 2\text{K soil} + Ca^{+2},$$

or

$$\frac{(\text{Na soil})(K^+)}{(\text{K soil})(Na^+)} = k, \quad \text{and} \quad \frac{(\text{K soil})^2(Ca^{+2})}{(\text{Ca soil})(K^+)^2} = k,$$

with the quantities in parentheses indicating concentrations. The term Na soil indicates that the sodium ion is exchangeable.

Vaneslow (1932) found that the activity of an exchangeable cation is proportional to its mol fraction in the material. He substituted mol fractions to express the activities of the reacting cations. His equation for the exchange between univalent and bivalent cations in a clay mineral is

$$\frac{\left(\frac{\text{K clay}}{\text{K clay} + \text{Ca clay}}\right)^2 [Ca^{+2}]}{\left(\frac{\text{Ca clay}}{\text{K clay} + \text{Ca clay}}\right)[K^+]^2} = \frac{[Ca^{+2}]\ (\text{K clay})^2}{[K^+]^2 \cdot \text{Ca clay}\ (\text{K clay} + \text{Ca clay})} = K.$$

Gapon (1933) developed an equation for the exchange between a liquid and a monomolecular layer of another liquid adsorbed on a solid. Representing the entire surface by F_0 and parts of the surface occupied by liquids C_1 and C_2 at equilibrium by F_1 and F_2, he gave the equation $\frac{C_1 \cdot F_2}{C_2 \cdot (F_0 - F_2)} = K$. Gapon considered that the amount of liquid that will be taken up by a solid through exchange will be proportional to the surface occupied by that liquid. This idea can be extended to include different kinds of cations in different exchange positions, and it fits in with the results obtained by Garrels and Christ (1956). The reaction for exchange of two kinds of cations is M_1 clay + M_2 $\rightleftarrows$ M_2 clay + M_1, where M_1 and M_2 are cations. At equilibrium, as in all mass-action equations, the velocity of the reaction to the right (V_1) equals the velocity to the left (V_2). This equation when applied to univalent cations is in the same form as given by Kerr (1928a; 1928b).

Jenny (1936) developed a kinetic equation for the exchange between cations of equal valence. He considered that each exchangeable cation oscillates about the center of a

electric charge on the surface of a particle. If a cation in a solution chances to pass between an exchangeable cation and the center of the electric charge, exchange takes place, and simultaneously an exchangeable cation becomes a solution cation. Jenny's equation is:

$$\frac{(K^+)(NaX)}{(Na^+)(KX)} = \frac{V_w}{V_b}$$

where V_w and V_b are the oscillation volumes of the two kinds of cations when in the exchangeable form, and X is the surface. This equation is equivalent to those given by Kerr (1928a, 1928b), Vaneslow (1932), and Gapon (1933).

Magistad and others (1944) reviewed the types of mass-action equations that have been formulated and worked out a number of equilibrium constants for NH_4^- and Ca exchanges in a soil. They used the equations of Vaneslow (1932) and Gapon (1933) and found that Gapon's equation agreed well with the experimental data.

Davis (1945a, 1945b) discussed theories of base-exchange equilibria and later studied ionic-exchange equilibria by applying the rules of thermodynamics (1950a; 1950b). The conditions for exchange reactions that he examined represent a Donnan equilibrium, and the equation that he derived is similar to that of Vaneslow (1932).

The mass-action law was applied by Garrels and Christ (1956) to explain the exchange reactions of beidellite (Putnam clay), "illite," and kaolinite by assuming that each clay mineral consists of two distinct substrates (H clays). Theoretically this is not strictly true, for the montmorillonites, in which group beidellite belongs, have three exchange sites, and "illites" also have three. Kaolinite has no definite number of exchange sites as the exchange is due to negative charges caused by broken bonds at the edges of the micelles.

One of the substrates (H clays) indicated by Garrels and Christ (1956) is due to the exchangeable cations within the mineral structure, whereas the other is due to the charge on the surfaces of the clay micelle. The curves obtained by titrating H clays with a base (Marshall, 1954) suggest that the part of the curve above pH 6 or 7 represents a distinct second clay acid. The dual nature of the neutralization of the charges on clay minerals has also been recognized by Jarusov (1937) and Schofield (1949a). The latter refers to the charge found between pH 2.5 and pH 5 or 6 as the "constant charge." However, this charge is apparently the same as the first H clay substrate.

By using Marshall's figures for the titration of H beidellite with KOH (Marshall and Bergman, 1942), Garrels and Christ (1956) calculated the constants for the two exchange sites:

$$(1) \qquad \frac{[KC]a_{H^+}}{[HC]a_{K^+}} = 10^{-2.5}$$

$$(2) \qquad \frac{[KE]a_{H^+}}{[HE]a_{K^+}} = 10^{-6.7}$$

where HC = first substrate H clay, KC = first substrate K clay, HE = second substrate H clay, and KE = second substrate K clay.

The following are values found for the exchange capacity at each of the sites:

$$HC_0 = 0.0835 \text{ moles}$$

$$HE_0 = 0.03815 \text{ moles.}$$

Calculation of the free-energy change for the reactions from the relation $\Delta F^0 = -RT \ln K$ gives

$$KC + H^+ \rightarrow HC + K^+;$$

$$\Delta F^0 = -3.4 \text{ kcal.}$$

$$KE + H^+ \rightarrow HE + K^+;$$

$$\Delta F^0 = -9.1 \text{ kcal.}$$

Thus the hydrogen ion is more strongly bonded to the E^- than to the C^- site

The exchange reaction under natural conditions—for example, a clay mineral in contact with a soil solution—is more complex because some exchangeable cations are more tightly held on the clay mineral than others, and the soil solution is generally a mixed electrolyte. In addition, at low pH values H clays lose Al^{+3} ions from the octahedral layer. These Al^{+3} ions occupy exchange sites in the clay minerals before they dissolve in the soil solution.

The equilibrium constants for three monovalent cations—potassium, sodium, and ammonium—reacting with beidellite, "illite," and bentonite have been calculated by Blackmon (1958, p. 739) as follows:

Ion	Beidellite		"Illite"		Bentonite	
	Low pH (C^-site)	High pH (E^-site)	Low pH (C^-site)	High pH (E^-site)	Low pH (C^-site)	High pH (E^-site)
K^+	−2.5	−6.7	−2.4	−5.7	−2.6	−8.0
Na^+	−3.2	−7.4	−2.8	−5.8	−2.9	−8.3
NH_4^+	−2.5	−6.9	−2.4	−5.7	−1.5	−5.4

The reactions are complicated by the bonding energies of the various cations and by the nature of the ionized surfaces as indicated by Marshall (1954). If a clay mineral is placed in contact with a homoionic or polyionic electrolyte the exchange reaction will depend on both the kind and concentration of cations in the solution and in the exchange positions of the mineral. The relationship of the first conditions is explained by Marshall's rule (1), whereas the exchange positions are covered by rules (2) and (3). The cations in the exchange positions of a clay mineral affect the relationship of any cations in a solution that is in contact with the mineral because some cations are exchanged preferentially with those in the solution. Thus, Mg^{+2} in sea water is adsorbed by montmorillonite, "illite," and halloysite preferentially to Ca^{+2}. Such changes in exchange cations are covered by rule (4). Variation in pH will cause a variation in the ratios of exchangeable cations in a clay mineral.

It has been shown that the clay minerals vary in the exchange sites—that is, in the number and position of places on the crystal lattice where an ion from a solution can be adsorbed. Also some ions are more firmly bound to the crystal lattice than others; the less firmly bound ions will, therefore, be those which are more readily exchanged, and ease of exchange is related to certain positions in the crystal lattice. Thus, according to Ganguly and Mukherjee (1951), kaolinite has two kinds of exchange positions, and mica and montmorillonite have three. As a consequence of the unequal surface-charge density and structure of the clay particles, it follows that the activity coefficient and the bonding energy of an exchangeable ion may vary from one spot to another—for example, for an ion held on a plane surface, on an edge or corner, or between inner surfaces of the layer minerals (Wiklander, 1955). However, there are definite groups of bonding energies that are related to the exchange sites in the 2:1 clay minerals. Kaolinite and halloysite have bonding energies that give rise to smooth curves on titration with a base. These titration curves indicate that the H forms of kaolinite and halloysite react as an infinite number of acids, whereas the H forms of montmorillonite and "illite" react as a mixture of two or three acids.

The replaceability of an exchangeable cation on a clay mineral differs with type of mineral, nature of other adsorbed cations, concentration of cations in solution, and pH. There is no universal order of replaceability of one cation with another. If univalent and bivalent cations are both present there is considerable variation with the nature of the exchanger and the concentration of the solution. Other factors are the exchange capacity and the degree of neutralization in relation to the solution concentration. Valence, ionic radius of the cations in nonhydrated and hydrated form, and polarizability and polarizing power are important factors (Wiklander, 1955, p. 137).

The adsorptive affinity increases with the valence. The less hydrated the cation, the more tightly it can be held. This agrees with the theory that the activity coefficient is affected by the radius of the hydrated ion.

The following ionic radii (in Ångstroms) are those given by Ahrens (1952) and Goldschmidt (1954):

Univalent: F, 1.36; Cl, 1.81; Li, 0.68; Na, 0.97; K, 1.33; Cu, 0.96; NH_4, 1.43; Ag, 1.26; Cs, 1.67

Bivalent: Mn, 0.80; Fe, 0.74; Co, 0.72; Ni, 0.69; Cu, 0.72; Zn, 0.74; Cd, 0.97; Hg, 1.10; Pb, 1.20; Be, 0.35; Mg, 0.66; O, 1.40; Ca, 0.99; Ba, 1.34

Trivalent: Cr, 0.63; Mn, 0.66; Fe, 0.64; Al, 0.51

Quadrivalent: Mo, 0.70; W, 0.70; V, 0.63; Si, 0.42; Ti, 0.68; Zr, 0.79

These ionic radii indicate how various cations can fit into the clay-mineral structures.

In addition to the exchange of single ions some polyions are adsorbed. Ions such as $CuOH^+$, $CuCl^+$, $ZnOH^+$, $FeOH^{+2}$, $Fe(OH)_2^+$ may be adsorbed either as polyvalent or as univalent ions. The mechanism of adsorption of the hydroxy cupric ion by clay minerals has been discussed by Menzel and Jackson (1951). The retention of hydroxy ions by clays is favored by lattice building of these ions onto the clay-mineral crystal.

Only a certain proportion of an ion in an exchange position on a clay mineral may be replaced with one from a solution. This is called the "symmetry value" by Jenny (1932). It is the percentage release of an exchangeable ion when a replacing ion is added in amounts equivalent to that of the adsorbed ion. Some symmetry values of bentonites allowed to remain in contact with various salts for 10 days at pH 7.55 are

	NaCl	KCl	NH_4Cl	$MgCl_2$	$CaCl_2$	$BaCl_2$
Na bentonite	....	63.6	54.5	82.4	87.8	88.0
K bentonite	34.0	....	48.5	71.6	....	60.0
NH_4 bentonite	32.7	49.1	....	73.8	78.8	78.6
Ca bentonite	11.4	25.2	20.2	40.4	....	47.7
Ba bentonite	11.5	23.5	21.8	44.3	46.4	....

The bivalent cations have a greater replacing power than do the univalent cations. In the preparation of heteroionic montmorillonite, or other clay minerals, the ion that is introduced first is more firmly bound than one that is introduced later. Bivalent ions are more strongly held than univalent ions. Montmorillonites occurring under natural conditions seldom have the exchange positions filled with only one kind of cation, although one may be dominant. The reaction of montmorillonites with ground water is, therefore, always complex.

Ross (1943) has stated the position with regard to the exchange phenomena in montmorillonite as follows:

"Experimentally almost any base or hydrogen may be exchanged for bases occurring naturally. Those occurring most widely are calcium, which is almost completely exchangeable, and sodium, which which is usually exchangeable but not always completely so. Small amounts of K, Mg, and even Al may be replaceable, as is hydrogen, which gives the clay an acid reaction. These ions differ greatly in their relative ease of replacement, which is represented by the following series:

$$Li < Na < H < K < Mg < Ca.$$"

Experiments have shown that both Mg and Ca are held in preference to Na if montmorillonite is soaked in sea water (Kelley and Liebig, 1934; Carroll and Starkey, in press).

There is little information available about the exchange of trivalent ions. The common cations Al^{+3} and Fe^{+3} do not enter into exchange reactions because they form insoluble hydroxides or oxides—$Al(OH)_3$ and $Fe(OH)_3$ are practically insoluble between pH 4.5 and pH 8, the range for most natural situations. The exchangeable Al^{+3} found in clay minerals at low pH values is a result of solution rather than a true exchange reaction. As Al^{+3} ions cannot be transported at the pH values of most soil solutions and ground waters, they accumulate and later crystallize as gibbsite or boehmite in bauxite and laterite deposits. The Fe^{+3} ions provide the red and brown oxides that coat mineral grains in soils, or they form indefinite iron oxides such as "limonite." The following trivalent and quadrivalent cations have been used in exchange experiments with clay minerals: cerium, lanthanum, thallium, and thorium. The trivalent cations are more strongly held by clay minerals than are the bivalent or univalent cations. Ukai and others (1958) have reported exchange reactions of thorium and uranium with montmorillonite, "illite," and kaolinite.

Effect of Environment on Cation-Exchange Capacity

The exchange of cations takes place in the thin film of water in contact with minerals. This is true for minerals like quartz and feldspar, the ferromagnesian minerals, and others, as well as for the clay minerals. There is considerable variation in the mechanism of exchange reactions resulting in the microscopic cancellation of negative charges on the surfaces of the minerals. In a general way, natural environments cause the presence or absence of certain cations in the circulating waters. In situations where the pH of the water seeping through soils is low (pH 4–5), the soil clay minerals tend to become H clays. In other situations where the water has an alkaline reaction, cations in the exchange positions of clays may be Ca, Mg, Na, K, or others. This relation between the exchangeable cations on the clay minerals and drainage water broadly separates soils into two great groups, the pedalfers and the pedocals. The same idea has been formulated by Millot (1949) as a result of his study of the clay minerals in sedimentary rocks that have been deposited in different environments.

The geological material present in any environment consists of rocks, soils, and unconsolidated materials modified by the solutions that circulate through them. The total effect of the environments causes the presence of certain clay minerals, and these in turn cause variation in the cation-exchange capacity of the material as a whole. The clay minerals found in a number of environments are given in Table 2.

Other Exchange Phenomena

Anion Exchange

Anion exchange is the exchange of an anion of a clay mineral with an anion in a solution in

TABLE 2.—OCCURRENCE OF CLAY MINERALS IN RELATION TO ENVIRONMENT

Mineral	Environment	Conditions of formation	pH	Approximate exchange capacity* m.e./100 g
Kaolinite	Soils, mineral veins	Leaching, oxidizing or reducing	4±	3–15
Halloysite	Soils, mineral veins	Leaching, particularly where oxidizing sulfides have supplied H_2SO_4; moist	3–4	5–10 ($2H_2O$)
Allophane	Soils, mineral veins	Similar to kaolinite or halloysite	4	70
Chamosite	Marine and in laterites		low	not known
Hydrous mica ("illite")	Soils and marine sediments; shales	Apparently fairly wide range of conditions; occurs as a transition type, but not under intense leaching; fixes K and other ions	not very critical	20–40
Glauconite	Marine	Near-shore environment, stagnant sulfide-containing waters	low	20
Celadonite	Alteration product	Various		not known
Montmorillonite group	Soils, bentonites, mineral veins, shales	Neutral or alkaline conditions; unstable under acid leaching	7+	80–100
Vermiculite	Soils, altered biotite	Apparently a fairly wide range conditions	not very critical	100–150
Chlorite	Rocks, soils, marine	Apparently a fairly wide range of conditions, but more stable in alkaline conditions	probably 7+	10–40?
Palygorskite	Lakes in arid environment	Dry, alkaline	8+	20

* Exchange capacity measured at pH 7.

contact with the mineral. It has been found, however, that the adsorption of anions by clay minerals involves in some cases replacement and in others addition (Marshall, 1949, p. 131). The site of the reaction is the exposed OH^- ions either on the planar surfaces or on the edges of the clay micelles. Kaolinite and halloysite have exposed OH^- ions in both situations, but montmorillonite and the micaceous clay minerals have exposed OH^- ions only on the broken edges. The anion-exchange capacity in kaolinite and halloysite is similar in amount to the cation-exchange capacity, but it is much less than the cation-exchange capacity in the other clay minerals.

The alkalinity of a clay suspension is increased by liberation of OH^- ions. Fluorine can replace the exposed OH^- ions because of comparable size. Both PO_4^{-3} and AsO_4^{-3} ions are adsorbed by kaolinite and by soils. Phosphate adsorbed on kaolinite can be displaced by arsenate (Dean and Rubins, 1947). The phosphate ions are adsorbed on the clay-mineral surface by sharing a hydroxyl position, and the PO_4^{-3} group projects from the surface. In strong acid solutions clays can take up both K^+ and Cl^- ions from a solution of KCl, and the Cl^- is exchangeable for other anions, and the K^+ for other cations (Schofield, 1949a).

The anions known to be adsorbed or exchanged on clay minerals are Cl^-, NO_3^-, SO_4^{-2}, PO_4^{-3}, and AsO_4^{-3}. They function as counter ions and are exchangeable with other anions in the same way as cations are exchanged (Wiklander, 1955, p. 141):

$$R{-}OH_2^+Cl^- + NO_3^- \rightleftarrows R{-}OH_2^+NO_3^- + Cl^-,$$

and

$$R{-}OH_2^+Cl^- + OH^- \rightarrow R{-}OH_2OH + Cl^-$$
$$\rightarrow R{-}OH + H_2O + Cl^-.$$

This mechanism of anion exchange explains why the exchange capacity for anions compared with cations is small in montmorillonite (few broken bonds compared to the charge induced by isomorphous replacement) and why the difference in the two capacities is less in kaolinite (both cation and anion exchange located at broken bonds). There is a higher anion-exchange capacity in soils than in clay minerals, because of the presence of hydrous ferric and aluminous oxides in soils. The mineralogical composition of clay colloids may be possibly determined by considering the ratio of the cation- and anion-exchange capacities. The following average ratio values have been obtained:

montmorillonite, 6.7;

"illite," 2.3;

kaolinite, 0.5.

Another type of anion exchange also occurs —namely, isomorphous displacement of OH^- from clay minerals and hydrous oxides:

$$R—OH + F^- = R—F + OH^-.$$

There is evidence that the phosphate ion, because it is not the same size as OH^-, is also bound as a structural nondiffusible unit by displacement of lattice OH^-. Because of differing bonding energy, the substitution for OH^- can occur at higher pH than the exchange of OH^-. Anion exchange is also complicated by the phenomenon of negative adsorption. The cations of a dilute neutral solution in contact with a clay mineral enter into exchange reactions with cations held to the mineral surface by negative charges, and this reaction may cause an increase in the concentration of the anions in the solution. Any excess positive charge on the mineral will be neutralized by the adsorption of anions from the solution. The mechanism of the replacement and the replacing powers of the various anions have been examined by Mattson (1932). A bentonite, Na saturated and equilibrated with various Na salts, showed negative adsorption in the order:

$$Cl^- = NO_3^- < SO_3^{-2} < Fe(CN)_6^{-4}.$$

McAuliffe and others (1947) found that radioactive phosphate ions in solutions replaced inactive phosphate ions from surfaces of minerals of several soils. Experiments with hydrated Fe and Al oxides and kaolinitic minerals showed exchange between deuterium-tagged hydroxyl ions in solution and ordinary hydroxyl ions on the hydrated oxide and clay-mineral surface. Humic acids also take part in anion exchange as shown by their power of releasing adsorbed phosphate, but the exact mechanism is not known.

Most of the information concerning adsorption and exchange of anions has been obtained from soils and not from individual clay minerals. Anion-exchange capacity is difficult to measure. It has been proposed to use the amount of phosphate ion adsorbed at pH 4 (Piper, 1947) or at pH 5.7 (Dean and Rubins, 1947) as a measure of the anion-exchange capacity.

Fixation of Cations and Anions by Clay Minerals

The principal cation fixed by clay minerals is potassium, but ammonium and barium are also fixed. The fixation of potassium was first noticed in soils where it is caused by the clay fraction. Reitemeier and others (1951) have reviewed the available information. The minerals in soils largely responsible for potassium fixation are the micaceous clay minerals because the K^+ ion is essential in the structure of these minerals. The effect of weathering on both muscovite and biotite is to reduce the amount of K^+ ion binding the mica sheets together, and the structure is weakened. The addition of K^+ ions increases the strength of the bonding between the sheets, and potassium is fixed. It has been shown that hydrous micas and all clay minerals that have been called "illites" can be wholly or in part regenerated to micas by the addition of K^+ ions. Kunze and Jeffries (1952) used potassium fixation as a measure of the amount of weathering that has taken place in soils containing micaceous clay minerals. The regeneration of hydrous micas by K^+ ions was measured by X-ray diffraction studies.

Recent work on a hydrous mica in Holland by Van der Marel (1954) has shown that a mineral which is described as "ammersooite," a potassium-fixing "illite," contracts its open-crystal lattice (d = 15.6 Å) when saturated with K, NH_4, Rb, or Cs ions—that is, with ions having a large polarizability. By such contraction, nonfixing common "illite" (Fithian), with d = 10.8 Å, is formed.

The importance of hydrous micas and "illites" as fixers of potassium in soils arises from the fact that they are the predominating

clay minerals of immature soils in temperate regions, and particularly of soils that are derived from shales, limestones, and glacial materials. Variation in micaceous clay-mineral content with parent rock in southern Scotland has been studied by Mitchell (1955).

Potassium fixation in vermiculite has been studied by Barshad (1948) who experimented with the adsorption of different cations and checked the results by X-ray and differential thermal analysis. The principal exchangeable ion in vermiculite is Mg^{+2} which is situated between the silicate layers and surrounded by six O^{-} atoms in 12 co-ordination. In addition, there are 8 water molecules. Only part of the K^{+} taken up by exchange from a solution could be replaced by NH_4^{+} (the ion commonly used for the determination of ion-exchange capacity), but Na^{+}, Mg^{+2}, and Ca^{+2} exchanged completely. As a result of the saturation with various ions it was found that the effect on the mineral structure, determined by X-ray diffraction, was

(1) The Mg-saturated (natural) material and the Ca-saturated mineral have a basal spacing (*d* 002) of 14.33 and 15.07 Å, respectively. There are 10 molecules of water per adsorbed ion which are lost between 0° and 150° C.

(2) The K-, NH_4-, Rb-, and Cs-saturated vermiculites have the narrowest spacing (10.42 to 11.97 Å) corresponding to one molecule of water which is lost between 0° and 600° C. The X-ray diffraction pattern of K-saturated vermiculite is identical with that of biotite. In this condition vermiculite reacts like biotite and will have a correspondingly small ion-exchange capacity.

(3) The Ba-, Li-, and Na-saturated vermiculites have a spacing which is intermediate between (1) and (2). The Ba-vermiculite has 6 water molecules, and the Li- and Na-vermiculite has 3 water molecules which are lost between 0° and 150° C.

(4) Upon complete dehydration at 750° C., the spacings of the Mg-, Ca-, Na-, Li-, and NH_4-saturated vermiculites approximate the spacing of talc (9.3 Å). The spacing of the Ba- and Rb-saturated mineral altered to that of biotite, and a small but significant change also took place in the Cs-saturated mineral, but there was little change in the K-saturated vermiculite.

(5) The property of exfoliation is lost by saturation with K, Rb, and Cs ions.

Thus, there is a very important relationship between the interlayer cation, the interlayer water, and the exchange capacity. The exchange process is reversible between Na, Ca, Mg, and K ions, but not completely between K, NH_4, Rb, and Cs ions. The latter behavior of the exchange process is known as "fixation." These can also be described as symmetry values following Ganguly and Mukherjee (1951). It should be noted that biotite can be changed to vermiculite by heating in solutions of $MgCl_2$.

Barshad's investigations have been given in some detail because they give one explanation for the fixation of K^{+} and NH_4^{+} in various clay materials which contain vermiculite and other micaceous minerals. Vermiculite and mixed-layer minerals are rather common as soil-clay minerals.

Ammonium is another ion which shows a strong tendency to fixation, especially in the deeper soil horizons. Allison, Kefauver, and Roller (1953) have shown that representative soils of the United States containing "illite" are able to fix some ammonium under moist conditions, but much on drying or heating. Vermiculite-containing soils are unique in that they fix about 70 per cent as much ammonium under moist conditions as when heated. Soils high in montmorillonite fix little ammonium when wet but a fair amount on heating. The NH_4 fixation is of the order of 1 m.e./100 g for moist surface soils to as much as 3.8 m.e./100 g in subsoils. This is probably due to the presence of organic matter in the surface soil and to the exchange status of the clay minerals present. Rodrigues (1954) also reported ammonia fixation in soils from British Honduras, Trinidad, and British Guiana.

The mechanism of ammonium fixation is not completely understood. It appears that NH_4^{+} can proxy for K^{+} and H^{+} in certain clay minerals, particularly the micaceous minerals in which a cation holds the layers together. The "illites," vermiculites, and possibly soil chlorites are the minerals most likely to fix ammonium. However, Nash and Marshall (1956b) have reported fixation in feldspars.

Phosphate is the principal anion fixed by clay minerals. In soils phosphate fixation is mainly due to the formation of insoluble salts of Fe, Al, or alkaline earths. Phosphates of Fe and Al seem to form at low pH, whereas phosphates of alkaline earths form at high pH values. Lateritic soils with abundant free iron and alumina are therefore very susceptible

to phosphate fixation. Because of the association of kaolinite with iron oxides in deeply weathered and leached soils phosphate fixation is more noticeable than in less mature soils. Three principal theories have been proposed to explain phosphate fixation. These are isomorphous substitution of P for Si in the tetrahedral structural units in clay minerals, adsorption at surfaces of a solid phase of phosphate ions from solution, and chemical precipitation whereby phosphate ions are removed from solution and bonded chemically to the mineral surface. Kittrick and Jackson (1956) have shown that chemical precipitation is the principal mechanism in phosphate fixation. Haseman and others (1950) reported the reaction of phosphates with hydrous oxides of iron and aluminum. The reaction mechanism is a rapid dissolution of a clay mineral—kaolinite—with the formation of a new phosphate precipitation in which definite minerals can be identified. Colloidal iron-oxide particles and aluminum hydroxide films react in a few minutes with phosphate solutions at room temperatures to form precipitates, but similar results are obtainable with kaolinite only after a few years at the same temperatures (Kittrick and Jackson, 1956, p. 82). The phosphate particles are extremely small when first formed but in about 2 years grow to sufficient size to be visible in a electronmicrograph. A number of different phosphate minerals have been identified by X-ray diffraction. The minerals formed depend on the cations associated with the phosphate and on the temperature and pH (Kittrick and Jackson, 1956).

Effect of Material Adhering to Clay-Mineral Surfaces

The exchange capacity of the clay minerals may be either increased or decreased by substances adhering to the flat surfaces of the particles. Organic ions penetrate between the layers in montmorillonite, vermiculite, and the hydrous micas. The expansion due to the penetration of glycol or glycerol between the layers in montmorillonite is the basis of an important technique in the X-ray identification of this group of minerals.

Ferric oxide adheres to the surfaces of clay minerals. Fripiat and Gastuche (1952) have studied the relation of ferric oxide and kaolinite in considerable detail. The so-called "free iron oxide" which can be readily removed from clay particles is situated on the external surfaces of kaolinite—that is, those containing the OH^- and the O^- ions, respectively. The nature of this iron oxide depends on the original state of the kaolinite; if the kaolinite has alkaline or alkaline-earth ions in the exchange positions, the structure of the kaolinite–iron oxide complex is compact, ordered, and nonporous; saturation of the surface is produced very rapidly, and excess iron oxide forms particles of pure oxide. If, on the other hand, the kaolinite is an H kaolinite, the resulting complex has a disordered structure, is porous, and has a capacity quasi indefinite for the adsorption of oxide. It was found that the quantity of Fe_2O_3 adsorbed on the kaolinite surface is about 10 times that of the exchange capacity—that is, if the exchange capacity is 5 m.e./100 g, then the quantities of iron fixed will be about 50 m.e./100 g.

One of the commonest features of tropical soils that have been leached by percolating water for considerable periods of time is the association of iron oxides with kaolinite. This association produces the predominant red coloration of these soils. If the weathering rock contains ferromagnesian minerals the iron is released. Iron is only very slightly soluble at pH 4 to 5, the values generally found in these soils. The iron is, therefore, precipitated on the surfaces of the clay minerals. The iron-oxide coating causes a reduction of the exchange capacity of kaolinite or halloysite, the clay minerals generally associated with tropical weathering, because it covers the exchange sites. The iron oxides also protect the kaolinite from further decomposition by percolating waters and provide sites for phosphate fixation.

Cation Exchange in Other Minerals and Materials

Zeolites

Zeolites have high exchange capacities (Table 3) that are caused by their structure. The structural framework of zeolites (Bragg, 1937, p. 251–265; Barrer, 1958, p. 101) is formed of polyhedra built by linking the simple fundamental units, tetrahedra of AlO_4 and SiO_4, in various ways. The polyhedra are stacked by sharing corners with neighboring groups. Channels occur within the structures.

> "In chabazite or gmelinite or in the felspathoids of nosean-sodalite type, eight channels radiate from the center . . . to the eight corners of the rhombic or cubic unit cell." (Barrer, 1958, p. 101).

The channels are arranged in different ways in the different zeolites. The diameters of the channels vary along their lengths. The following are diameters given by Barrer (1958, p. 101):

	Maximum diameter (Å)	*Minimum diameter (Å)*
Chabazite	7.3	3.2 2.2
Faujasite	12	9

The zeolites are characterized by the fact that they contain very loosely held water which can be removed by heating and regained on exposing to a moist atmosphere. The water can be replaced by other substances such as ammonia, carbon dioxide, alcohol, mercury, or iodine. The cavities in the framework of tetrahedra contain positive ions, generally alkali or calcium ions, that balance the negative charge of the framework caused by unfilled positions. Marshall (1949, p. 27) has listed the framework-charge ratios, Al/Al + Si, for a number of zeolites. These ratios range from 0.167, in heulandite to 0.500 in thomsonite.

In analcime or in other zeolites, the possibility of cation exchange is due not only to channels in the structure but also to the presence of water and the existence of alternative empty positions in the neighborhood of each Na^+ ion. Diffusion of the Na^+ ion is more probable when only two-thirds of the available positions are filled than when all are filled.

Water molecules are always associated with the framework cations. The zeolite structures belong to three main divisions:

(1) Fibrous zeolites, such as natrolite, $Na_2(Al_2Si_3O_{10})\cdot 2H_2O$, consist of chains of linked tetrahedra in which the binding is strong.

(2) Lamellar zeolites, for example heulandite, $Ca(Al_2Si_7O_{18})\cdot 6H_2O$, consist of sheets in which the linking is strong and which are bound together by weak links, perhaps only cations and water.

(3) Analcime and chabazite, cubic and rhombic, respectively, consist of 3-dimensional frameworks of fourfold and sixfold rings of tetrahedra.

Barrer and Hinds (1953) have reported interesting experiments on the ion exchange in analcime and leucite with replacements of the following ion pairs: Na-K, Na-Tl, Na-Rb, K-Tl, Tl-Rb, and Na-Ag. The exchange isotherms for Na-K, Na-Tl, and K-Tl showed evidence of limited mutual solubility of the end members in the exchange. The analcime framework does not give ideal solid solutions of one cationic form in another; one reason for this is that the aluminosilicate framework undergoes small but definite readjustments according to the nature of the interstitial cations and to whether they are hydrated or not.

Another feature of the exchange phenomenon in analcime is ion-sieve action. The ions Na^+, Ag^+, K^+, NH_4^+, Tl^+, and Rb^+ with radii of 0.97, 1.26, 1.33, 1.43, 1.47, and 1.47 Å, respectively, can diffuse into analcime crystals, but Cs (radius 1.67 Å) cannot. It follows that the Na^+-K^+ exchanges—that is, analcime to leucite—are easily established, but that the Na^+-Cs^+ and K^+-Cs^+ equilibria cannot be established. Another interesting feature is that the interstitial channels are not everywhere of the same diameter and are not wide enough for the passage of the larger ions. The exchange relations of another zeolite, mordenite, have been investigated by Barrer (1948). Mordenite also acts as a molecular sieve. The diameters of the interstitial channels in natural mordenite are just a little more than 4.0 Å at their narrowest parts. The ionic diameters of certain exchanging cations and anions are

Ion	Li^+	Na^+	K^+	NH_4^+	Ca^{+2}	Ba^{+2}	Cl^-	NO_3^-
Diameter (Å)	1.20	1.90	2.66	2.86	1.98	2.70	3.62	5.10

Thus, the cations can diffuse readily into the lattice; the chloride ion might just enter, but the nitrate ion could not unless the lattice recrystallized.

Vaneslow (1932) gives figures of about 295 m.e./100 g for heulandite and 420 m.e./100 g for analcime. Figures given by Barrer (1958) for various zeolites are listed in Table 3. Interest in analcime and mordenite arises from the fact that these minerals are found in beds in certain formations in the western United States—for example, the Popo Agie member of the Chugwater formation (Triassic), the Green River formation (Eocene) in Wyoming, and the Barstow formation (Miocene) of the Mojave Desert. The zeolites remain stable under dry, alkaline conditions but alter under moist conditions.

Rocks and Minerals

The only rock-forming minerals that have high ion-exchange capacities are the fels-

TABLE 3.—CATION-EXCHANGE CAPACITY OF VARIOUS MINERALS AND ROCKS

Mineral or rock	Grain size (μ)	Cation-exchange capacity (m.e./100 g)	Source
Feldspar	0.5–1.0	1.0–2.0	Nash and Marshall (1956b)
Felspathoids			
Leucite	....	460	Barrer (1958)
Sodalite	....	920	
Nosean	....	880	
Cancrinite	....	1090	
Pyrophyllite	....	4.0	Kingery and others (1955)
Quartz	2–62	0.6	Ganguly (1951)
Quartz	<2	5.3	Ganguly (1951)
Talc	0.5–5	0.2	Kingery and others (1955)
Zeolites			
Analcime	....	450	Barrer (1958)
Chabazite	....	400	
Edingtonite	....	390	
Faujasite	....	390	
Gmelinite	....	400	
Harmotome	....	390	
Heulandite	....	330	
Levynite	....	400	
Mordenite	....	230	
Natrolite	....	530	
Scolecite	....	500	
Stilbite	....	320	
Thomsonite	....	620	
Basalt	60–120	2.8	Snake River basalt, Idaho. Analyst, D. Carroll
Basalt	<2000	0.5	
Pumiceous tuff	<62	1.2	Tsherege member of Bandolier tuff, New Mexico. Analyst, D. Carroll
Shale	>62	41.0	Pierre shale, Cretaceous, various localities; average 61 samples (including bentonite beds and various types of shale). Analysts, D. Carroll and H. C. Starkey
Shale	>62	10.0	Conosauga shale, Cambrian; average 28 samples, fresh and weathered rock. Analyst, D. Carroll
Tuff	>62	32.0	Barstow formation, Miocene, Mojave Desert; average 6 samples containing zeolites. Analyst, D. Carroll
Tuff	<2	49.0	

pathoids. Barrer (1958) has given figures for the ion-exchange capacity of various members of the felspathoid group (Table 3). The importance of the high exchange capacity of these minerals in weathering processes has not yet been evaluated.

There are several factors to be considered in discussing the ion-exchange status of rocks. The most important are porosity and grain size, constituent minerals, and solutions taking away or supplying cations. In general, leaching solutions are acid and cause the removal of metal cations. A rock must be sufficiently porous for ion-containing solutions to circulate to the minerals in which ion exchange might be expected to occur.

Some rocks when in sufficiently small disaggregated grains have a low cation-exchange capacity—for example, powdered basalt or pumice (Table 3). Fresh rocks have a lower

exchange capacity than altered or weathered rocks. The Snake River basalt, for example with a glassy groundmass when fresh has an exchange capacity of 0.5 m.e./100 g for large particles, but when the groundmass is altered chemically and changed to a clay mineral the exchange figure is much higher.

Fine grains of all inorganic materials have a small cation-exchange capacity as a result of broken bonds around their edges. For fine-grained minerals the figure is about 1–3 m.e./100 g. The smaller the grain size the greater the surface area; thus, a sphere 1 cm in diameter has a surface area of 3.14 cm^2. If the sphere is broken into particles the size of colloidal clay ($<2\ \mu$) there would be 8×10^9 particles with a surface area of 6283 cm^2 (Baver, 1940). Ganguly (1951) has given the exchange capacity of quartz $<2\ \mu$ as 5.3 m.e./100 g and of particles 2–62 μ as 0.6 m.e./100 g. This is of interest because many clay fractions of soils contain quartz in varying proportions, and it seems that an appreciable part of the exchange capacity of such fractions may be due to quartz and not to the clay minerals present.

The exchange reactions of the surface of feldspar have been studied by Nash and Marshall (1956a; 1956b). They found that there is no consistent order of release of cations by the different feldspars when acted on by HCl. They state, "There is a different order of release for each of the solutions used and for each cation displaced." (1956a, p. 33–34). There is no relation between the amount of cation released and the total amount present in the mineral. In salt solutions, the release of cations from feldspar is apparently a complex process. It is suggested (Nash and Marshall, 1956b, p. 36) that between the external surface and the unchanged feldspar there exists a relatively thin layer of adjustment or accommodation. This layer apparently fixes ammonium strongly, possibly by adsorption of NH_3 thereby releasing one H^+ ion for further penetration. Cation-exchange capacities for feldspars range from 2 to less than 1 m.e./100 g for particles of 0.5–1.0 micron size.

Another kind of cation exchange that can take place in minerals and rocks is contact exchange. It is presumed to occur by direct contact which causes the intermingling of the double layers in the thin films of water surrounding the minerals. Every ion held at a negative spot on the clay (or mineral) surface is supposed to have a certain oscillation volume around this center. The volume increases with ion hydration and decreases with valence so that it can be correlated with adsorption affinity. If the oscillation volumes overlap, ions may migrate along the exchange surface, or they may exchange with ions on an adjacent particle. Contact exchange and surface diffusion are probably very important in rock weathering and soil formation.

Organic Matter and Organic Complexes

The cation-exchange capacity of organic matter is high. Values of 150 to 500 m.e./100 g have been reported for the organic matter of some soils (Grim, 1953, p. 132). Hosking (1948, p. 49) found a range of 120 to 190 (average 170) m.e./100 g for the organic matter in a number of Australian soils. Humic acids give an additional negative charge to the clay particles with which they are associated. Organic matter present in soil seems to form a complex with the clay minerals, principally in the surface layers of the soil. This increases the cation-exchange capacity considerably. The most comprehensive study of the cation-exchange capacity of organic matter in soils is that of de Leenheer and Appelmans (1953) on the exchange capacity of the polder clays and of the Schelde alluvium. In this investigation the exchange capacity of the organic matter was obtained from the total exchange capacity and the exchange capacity of the mineral fraction of the soil using the following formula:

$$\frac{To = 100Tt - Tm[100 - (v + h)]}{h},$$

where To = exchange capacity of organic fraction; Tt = total exchange capacity; Tm = exchange capacity of the mineral fraction; v = moisture content of air-dried sample; and h = content of organic material (determined with H_2O_2). Application of this formula was simplified by using prepared graphs.

Organic ions such as amines can enter into exchange reactions with clay minerals (Slabaugh, 1954) forming organic-clay complexes. Slabaugh gives the following quantities of amine ions adsorbed on Wyoming bentonite (in the Na form with an exchange capacity of 92 m.e./100 g) by exchange reactions:

AMINE

(Concentrations are in millimoles per liter of bentonite suspension)

Sample no.	CH_3	C_4H_9	C_8H_{17}	$C_{10}H_{21}$	$C_{14}H_{29}$	$C_{18}H_{37}$
2	0	0	0	0	0	0
3	0	0	0	0	0.1	0
4	0	0	—	0.18	0.41	0.40
5	—	0	0.10	0.49	0.92	1.00
6	0	0	0.20	2.9	3.2	3.4
7	0.02	0.14	0.70	3.5	5.5	5.9
8	0	0.55	0.97	3.9	6.6	9.1
9	0.35	3.2	—	3.6	6.8	25
10	0.20	3.3	—	3.5	6.7	—

The exchange reaction between Na-bentonite and organic amine hydrochlorides is assumed to be the following:

$$\text{Na bentonite} + \text{R NH}_3^+ \rightarrow \text{Na}^+ + \text{R NH}_3 \text{ bentonite}$$

The amine-bentonite was made by adding the amine to hydrogen bentonite which was prepared by passing the clay suspension through an Amberlite IR-120 column in the acid form. On the exchanger (bentonite) the amine ion distributes itself between the cationic exchange sites, where it releases an equivalent amount of sodium ion, and the adsorption sites.

Thus, when an amine ion exchanges with the sodium ion in the clay, four factors are involved:

(1) The Na^+ ion is dissociated from the clay going into true solution.

(2) The amine ion leaves the solution phase and becomes associated with the colloidal clay particle.

(3) The amine ion becomes oriented about the exchange site, its ionic charge balanced by the charge on the clay lamina.

(4) The hydrocarbon chain of the amine is absorbed onto the clay laminar surface accompanied by the removal of the water which was previously adsorbed on this surface.

The results of this experimental work have an important bearing on the nature of the relations between organic matter and clay minerals in soils. Further, since it is known that amines persist in sedimentary rocks, such as limestones containing organic remains, it is possible that exchange reactions of this type may take place within such rocks and within their disintegration products leading to soil formation. Small quantities of clay minerals, especially "illitic" or montmorillonitic, occur in limestones.

Amorphous Material

Silica gel is amorphous and possesses an open structure; hence, it offers a much greater active surface than powdered quartz (Ganguly, 1951). Prepared dry-ground silica gel has an exchange capacity of 80 m.e./100 g because of the availability of exposed OH groups. When the gel is ignited the exchange capacity is reduced to approximately that of quartz of similar grain size, to which it has probably changed on ignition (900° C). Robertson and Twedily (1953) give information about the exchange capacity of diatomaceous earths from Skye and Kenya which contain amorphous gel material. The exchange capacities were 54, 25, and 31 m.e./100 g. The cation-exchange capacity of the gel material in the Skye diatomite was 74.7 and 98 m.e./100 g. It is probable that amorphous material of varying composition will add to the cation-exchange capacity of the rocks in which it occurs, and may perhaps be fairly common in weathering rocks—for example, in basalt which contains a glassy groundmass.

Treatment of many clay minerals in strong acids or alkalies causes a partial breakdown of their structure and the release of alumina or silica in an amorphous form. The minerals then have increased exchange capacities that can be made use of commercially (Nutting, 1935; 1937).

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SIGNIFICANCE OF ACCUMULATOR PLANTS IN ROCK WEATHERING

BY T. S. LOVERING

PREFACE

This is a review paper only in the sense that much pertinent biochemical literature is reviewed for its bearing on the thesis that accumulator plants are important geologic factors, a proposal first made in 1958 (Lovering, 1958). I am not a "biogeochemist", and the ideas presented here must stand on their own feet—but at least they have the merit of being uninfluenced by current dogma in the fields discussed. I am, however, deeply indebted to many friends in these fields for suggestions, especially as to the vast and unfamiliar literature; and foremost among these helpful guides, I am happy to acknowledge the indispensable aid given to me by H. W. Lakin, soil scientist, geochemist, and currently chief chemist of the geochemical exploration section of the U. S. Geological Survey. Although I stress evidence for the conclusion that vast quantities of SiO_2 are pumped out of the ground by silica-accumulator plants, which sooner or later release the silica in a form very vulnerable to physical transport by runoff or wind erosion, it should be made clear that we cannot yet appraise the value of this concept until much field work is done. I am not yet persuaded that erosive agents remove the major part of the vegetal silica in the tropics—or elsewhere—but I am convinced that this possibility must be given a serious study. At present we have absolutely no quantitative data on the relative amounts of silica taken up by various plant communities, nor any factual information as to the proportions of such silica recycled by plants, dissolved, and moved down into ground water, swept off the surface by erosive agents, or left behind as an insoluble residue from decaying plant litter. And I believe we should set about getting this information.

ABSTRACT

Accumulator plants differ widely in the elements accumulated but have been studied chiefly for their capacity to pick up minor elements deleterious to agriculture. However, the ability of some plants to accumulate certain major elements, such as silicon, aluminum, calcium, manganese, and iron, has geologic implications. Many kinds of vegetation, especially in the tropics, contain several per cent silica dry weight. Some 10 to 20 tons dry weight of new growth per acre is added each year above ground in tropical jungles, and the roots add several tons more. A forest of silica-accumulator plants averaging 2.5 per cent silica and 16 tons dry weight new growth per year would extract about 2000 tons of silica per acre in 5000 years—equivalent to the silica in 1 acre-foot of basalt. Comparison of lateritic soils with parent rock indicates that a silica-accumulator jungle could convert basalt into lateritic soil rapidly—geologically speaking. The silica in ground water increases with depth and time in contact with the rock, but vadose water seems inadequate to yield the silica required by such a jungle of silica-accumulator plants; biochemical factors must therefore cause much more rapid solution of silica. Under favorable conditions, much soluble organically derived silica may be recycled or added to ground water, but nevertheless, in tropical regions with high rainfall and appreciable runoff, large amounts of siliceous organic debris must be swept off the forest floor into the drainage system. On the other hand, if insoluble silicic phytoliths result from the disintegration of the vegetal litter, the upper soil horizons may become enriched in silica from disintegrating silica-accumulator plants, where erosion does not equal the rate of accumulation, as in many prairie and savannah soils. Plants that accumulate other elements, such as calcium, aluminum, manganese, or iron, may have geologic importance in developing other special soil types and in expediting the selective removal of certain elements.

SOMMAIRE

Les plantes accumulatrices de minéraux varient beaucoup quant aux élements accumulés, mais ont été étudiées surtout en raison de leur capacité d'absorber des élements

secondaires nocifs pour l'agriculture. Cependant la faculté qu'ont certaines plantes d'accumuler certains éléments importants tels que silicium, aluminium, calcium, manganèse et fer a une portée géologique. De nombreux types de végétation, notament dans les tropiques contiennent un pourcentage de plusieurs unités de silice en poids sec. De 25 à 50 tonnes (poids sec) de matière végétale nouvelle s'ajoutent par hectare et par an audessus du sol dans la végétation tropicale, et les racines en ajoutent encore plusieurs kilogrammes.

Une forêt de plantes accumulatrices de silice contenant une moyenne de 2,5 % de silice et produisant 40 tonnes (poids sec) de matière végétale nouvelle par hectare et par an extrairait à peu près 1 tonne de silice par hectare et par an, soit l'équivalent de la silice contenue dans le profondeur d'un m. de basalte pendent 16,000 ans. Si l'on compare les sols latéritiques avec la roche-mère, on voit qu'une végétation de plantes accumulatrices de silice pourrait transformer le basalte en sol latéritique très rapidement—à l'échelle géologique.

La quantité de silice contenue dans l'eau du sol augmente avec la profondeur et la durée du contact avec la roche, mais l'eau vadose ne parait pas suffire à fournir la silice nécessaire à une telle végétation de plantes accumulatrices; des facteurs biochimiques doivent donc provoquer une dissolution beaucoup plus rapide de la silice. Dans des conditions favorables, beaucoup de silice d'origine organique peut être re-introduite dans le cycle ou ajoutée à l'eau du sol, mais d'autre part, dans les régions tropicales à fortes pluies et ruissellement intense, de grandes quantités de débris organiques siliceux doivent être enlevés au sol de la forêt et emportés par le réseau de drainage. D'un autre côté, si des phytolithes de silice insoluble demeurent après la désintegration de la litière végétale, les couches superficielles du sol peuvent être enrichies en silice par la désintegration de plantes qui l'accumulent, là où l'érosion est inférieuce à la vitesse d'accumulation, comme c'est le cas dans le sol des prairies ou savannes. Les plantes qui accumulent d'autres éléments tels qui calcium, aluminium, manganèse ou fer peuvent avoir une importance géologique dans la formation d'autres types spéciaux de sols, ou en accélerant l'enlèvement selectif de certains éléments.

Zusammenfassung

Speicherpflanzen unterscheiden sich weitgehend durch die aufgespeicherten Elemente. Sie sind hauptsächlich auf ihre Fähigkeit untersucht worden, untergeordnete Grundstoffe aufzunehmen, die für den Ackerbau schädlich sind. Jedoch hat die Fähigkeit einiger Pflanzen, bestimmte Grundelemente wie Silizium, Aluminium, Kalzium, Magnesium und Eisen aufzunehmen, geologische Folgerungen. Viele Pflanzenarten, besonders in den Tropen, enthalten mehrer Prozente Silikat im Trockengewicht. In den tropischen Urwäldern werden in jedem Jahr einige 10 bis 20 Tonnen Trockengewicht per Acre durch frisches Wachstum oberhalb des Bodens hinzugefügt, und die Wurzeln fügen etliche Tonnen mehr hinzu. Ein Wald von Silikat-auf-speichernden Pflanzen, der durchschnittlich 2,5% Silikat, das sind 16 Tonnen Trockengewicht per neues Wachstum pro Jahr ansammelt, würde etwa 2000 Tonnen Silikat pro Acre in 5000 Jahren heraus ziehen, das entspricht dem Silikatgehalt in einem fußtiefen Acre von Basalt. Ein Vergleich zwischen lateritischen Böden und ihrem Muttergestein zeigt, daß-geologisch gesprochen-ein Silikat aufspeichernder Urwald Basalt schnell in lateritischen Boden verwandeln könnte. Im Grundwasser nimmt das Silikat mit der Tiefe und der Zeit, während der es in Kontakt mit dem Gestein ist, zu. Vadoses Wasser scheint jedoch nicht ausreichend zu sein, um die genügende Menge an Silikat, die durch solch einen Urwald von Silikat aufspeichernden Pflanzen benötigt wird, zu liefern. Biochemische Faktoren müssen deshalb eine viel schnellere Lösung von Silikat hervorrufen. Unter günstigen Bedingungen können viele lösliche Silikate, die von organischen Bestandteilen abstammen, dem Kreislauf, oder dem Grundwasser, sieder zugefügt werden, aber trotzdem müssen in tropischen Gebieten mit viel Regen und merkbarem Gefälle große Mengen von kieselhaltigen organischen Überbleibseln von den Waldböden in das Drainage-System geschwemmt worden sein. Andernfalls, wenn unlösliche, kieselhaltige, organische Gesteine von der Disintegration pflanzlicher Reste herrühren, könnten in oberen Bodenhorizonten Silikate von den widerstandsfesten kieselsäure-speichernden Pflanzen angereichert werden, und zwar dort, wo die Erosion nicht so groß ist wie die Aufspeicherung, ebenso wie in vielen Prärie-und Savannenböden. Pflanzen, die andere Grundstoffe, wie Kalzium, Aluminium, Magnesium oder Eisen aufspeichern, können geologische Bedeutung erlangen, indem sie andere, spezielle Bodentypen entwickeln, und indem sie die selektive Beseitigung bestimmter Grundstoffe beschleunigen.

ГЕОЛОГИЧЕСКОЕ ЗНАЧЕНИЕ РАСТЕНИЙ АККУМУЛЯТОРОВ В ВОПРОСЕ ВЫВЕТРИВАНИЯ ПОРОД

Т. С. Ловеринг

Абстракт

Растения аккумуляторы сильно различаются согласно аккумулированными ими элементами, но изучались они главным образом в виду их способности подбирать второстепенные элементы вредные для земледелия. Однако способность некоторых растений аккумулировать некоторые главные элементы, как то, кремний, алюминий, кальций, марганец и железо касается уже геологии. Многие типы растений, особенно в тропических странах, содержат несколько процентов кремнезема по сухому весу. Около 10 до 20 тонн /сухой вес/ новых всходов на акр прибавляется каждый год на поверхности земли в тропических джунглях, а кроме того несколько тонн добавляется корнями этой растительности.

Лес растений аккумуляторов, содержащих в среднем 2.5% кремнезема и 16 тонн /на сухой вес/ нового ежегодного всхода должны поглотить около 2000 тонн кремнезема с акра земли в течении 5000 лет, что равносильно содержанию кремнезема в одном акр-футе базальта.

Сравнение содержащей железо почвы с оригинальной породой показывает, что кремнезем аккумулирующие джунгли могли быстро /в геологическом смысле/ превратить базальт в эту почву. Количество кремнезема в грунтовой воде увеличивается с глубиной и временем контакта с породой, но вода верхнего слоя почвы повидимому неспособнадать количество кремнезема, требуемое такими кремнезем аккумулирующими джунглями; таким образом биохимические факторы должны способствовать более быстрому растворению кремнезема.

При благоприятных условиях хорошо растворимый органически образованный кремнезем может быть возвратимым циклом прибавлен к грунтовой воде. Тем не менее в тропических областях при сильных дождях и большом стоке воды большие количества содержащих кремнезем органических дебрей должны быть смыты с поверхности земли леса в водосточную систему.

С другой стороны, если нерастворимые содержащие кремнезем слои образуются от распада растительного мусора, верхние слои почвы могут быть обагащены кремнеземом путем распада кремнезем аккумулирующих растений в местах, где скорость эрозии не равна скорости накопления, как то имеет место в почвах прерий и саванн.

Растения, которые аккумулируют другие элементы как то кальций, алюминий, марганец и железо, могут иметь важное значение в образовании других сортах почвы и способствовании отборному удалению некоторых элементов.

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Introduction

Much experimental work has been done to ascertain the effect of various types of inorganic solutions on rocks and minerals, and the probable relevance of this work to weathering processes has been pointed out. It is also generally recognized that biochemical factors are important in surficial processes, but, so far as the writer is aware, it has not been realized that accumulator plants may withdraw from soil and rock geologically significant amounts of various elements, which may then be largely eliminated by surface runoff, wind, or solution. An accumulator plant may be defined as one that takes up certain specific elements from its environment in unusual amounts—tending to accumulate them rather than to discard or refuse them.

Plants that selectively accumulate elements that are toxic or harmful to livestock or agricultural production—such as selenium, molybdenum, sulfur, fluorine, zinc, and other minor elements—have caused concern for many years, and this has led to extensive studies. Comparatively few papers have been written about plants that accumulate the common elements silicon, aluminum, manganese, and iron—the abundance or poverty of which elements determine many major soil types—but there is a wealth of literature on the requirements and physiological response of plants to phosphorus, calcium, potassium, and many trace elements.

Silica-Accumulator Plants

The amount of silica accumulated by certain plants through biochemical processes is sufficiently large to warrant consideration of the possible *geologic* importance of this type of activity. It is well known that many hardwoods, grasses, reeds, bamboos, palms, corn, and horsetail or scouringrush take up an unusual amount of silica (Table 1). Some species of *Equisetum* (horsetail), sedge, reeds, and bamboo contain about 10 per cent SiO_2 (dry weight), and grasses are notoriously high silica forage plants. Parker (1957) has shown that blue grama grass and threadleaf sedge may have 10 per cent SiO_2 (dry weight) in the winter; rye grass contains about 3.5 per cent, and the leaves of corn about 2.5 per cent SiO_2. Sugar cane takes up about 1700 pounds of SiO_2 per acre in 2 years in Hawaii (Moir, Hance, *et al.*, 1936, p. 134).

Many tropical timber trees and also some of the temperate-zone hardwoods are silica accumulators. Laiseca (1949, p. 88) records 83.3 per cent SiO_2 in the ash of Persian Walnut, *Juglans regia*, and gives a table (p. 18) showing a steady increase in the silica content of the ash of beech leaves from 1.2 per cent in May to 25 per cent in November; Wolff (1880) records somewhat more—about 35 per cent SiO_2 in the ash of October leaves or approximately 2.5 per cent dry weight; according to Amos and Dadswell (1949), more than 375 species of tropical timber trees must be classed as silicic—*e.g.*, containing more than 0.05 per cent SiO_2 dry weight. Some of them, such as *Eschweilera odora* (Poepp), a tree common in Dutch Guiana and British Guiana, and *Antidesma ghaesembilla* (Gaertn) from New Guinea, may contain more than 3.5 per cent SiO_2 dry weight, but individual specimens may have very much less (Amos, 1952). The wood of *Antidesma pulvinatum* (Hillebrand), a tree endemic to Hawaii and near-by islands, contains 2.97 per cent SiO_2 based on the original wood (Wise, 1951). Many species of the tropical hardwoods range between 2 and 3 per cent dry weight SiO_2. According to Amos (1952), nine species of *Licania* average 1.5 per cent SiO_2 (dry weight), and three contain from 2.4 to 2.8 per cent SiO_2. Besson (1946) found 3.0 per cent in one species—81.2 per cent SiO_2 in the ash!

S. Linné, who has made a study of the use of biological silica as an ingredient of South American pottery (Linné, 1932), notes that siliceous plants are common in tropical America, especially in Brazil, where the genera *Chrysobalanus*, *Moquilea*, *Grangeria*, *Hirtella*, *Lecostemon*, *Licania*, and *Turiuva*—all belonging to the family Rosaceae and all rich in silica—are widespread in the Amazon Basin. The bark of the "Caraïpé tree" (*Moquilea*) is incinerated by the Indians, and the ash is added to the local clays used in making pottery to prevent undue shrinkage and cracking. The heavy bark of this tree is about 50 per cent SiO_2 (dry weight), but no analyses of the other

parts of this singular tree are available; the analyses of woods from the related genus *Licania*, cited above, suggest that the tree could be one of the premier silica accumulators of the plant kingdom. Commonly the foliage of trees and other plants is richer in silica and alumina than are the trunk, stem, and branches. Küster (1897b) states that siliceous secretions or bodies ("Kieselkörper") are characteristically present in *Chrysobalanus* trees. They are especially common in the mesophyll layer of the foliage but may be present either in the woody parts or in the leaves or in both.

TABLE 1.—ANALYSES OF SOME SILICA- AND IRON-ACCUMULATOR PLANTS

(Arranged in order of decreasing silica content, dry weight)

	Per cent SiO_2 in dry weight	Ash: per cent of dry weight	Weight per cent in ash								
			SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5	SO_3	Cl
Giantreed, *Arundu donax* (leaves)[1]	9.5	12.5	76.9,	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Common gromwell, *Lithospermum officinale*[2]	8.11	29.30	27.68	n.d.	0.28	3.15	59.01	0.77	6.17	2.17	0.77	n.d.
Water chestnut, *Trapa natans*[3]	5.53	19.62	28.00	n.d.	26.51	6.36	16.28	2.06	6.47	n.d.	2.63	0.55
Giant horsetail, *Equisetum telmateia* (Ehrh.)[4]	5.40	17.39	31.08	0.96	23.39	2.20	13.50	1.41	9.26	1.26	8.95	6.12
Giantreed, *Arundu donax* (stems)[1]	3.9	5.5	70.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
English ryegrass, *Lolium perenne* L.[5]	3.46	12.12	28.51	n.d.	1.04	2.34	10.15	1.26	37.80	9.64	5.78	5.57
Bluegrass, *Poa maritima*[2]	3.23	6.81	47.48	n.d.	4.58	2.99	4.28	10.05	11.37	4.42	1.75	11.09
Gris-Gris, *Licania* sp.[7]	3.59	2.97	81.19	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Chinalaurel, *Antidesma pulvinatum* (Hil.)[6]	2.97	4.26	69.72	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Palm, *Calamus rotang*[2]	2.15	3.16	67.96	n.d.	0.33	11.81	16.97	0.56	0.65	0.29	0.76	n.d.
Field horsetail, *Equisetum arvense* (L.)[4]	0.37	6.05	6.19	n.d.	37.35	6.90	19.80	7.72	4.26	2.87	6.78	5.49

[1] Collector and analyst—Celeste Engel, U. S. Geological Survey, Pasadena, California, February 1958.
[2] Emil Wolff (1880, p. 110, 111, 121), single analysis.
[3] Emil Wolff (1880, p. 133), average of 2 analyses.
[4] Giovanni Mariani (1888, p. 71, 73), individual analysis.
[5] Emil Wolff (1880, p. 121), average of 11 analyses.
[6] L. E. Wise (1951, p. 70), wood samples from Hawaii.
[7] A. Beeson (1946), wood from Guatemala.
n.d. = not determined

ALUMINUM- AND IRON-ACCUMULATOR PLANTS

As has been pointed out by Hutchinson (1943), the average content of aluminum in terrestrial vegetation is comparatively low, approximating about 0.02 per cent of the dry weight, and almost none has been found in any of the composites; there are, nonetheless, many aluminum-accumulator plants that carry an extraordinarily large percentage of this element. (*See also* Chenery, 1948.) Some of Hutchinson's data, summarized below, indicate the general range of aluminum content and the variety of plant families in the aluminum accumulators.

	Per cent Al_2O_3 in ash
Silky oak, *Orites excelsa*	36–80
Sweetleaf, *Symplocos*	40–51
Dwarf evergreen (Diapensiaceae)	40–51
Club moss, *Lycopod*	30–49
Spurge (Euphorbiaceae)	23–27
Tree fern, *Cyathea medullaris*	20
Linden (Tiliaceae)	20∓
Hickory, *Carya* or *Hicoria*	9–10
Camellia (Theaceae)	5–10
Oak, *Quercus mirilandica*	6
Shortleaf pine, *Pinus echinata*	5

A remarkable tree, the silky oak *Orites excelsa* of Australia (not a true oak, and misidentified as the sheoak by Smith according to Hutchinson), actually secretes aluminum succinate in cavities in the wood, and its ash is about three-fourths Al_2O_3, but I have seen no analyses of other representatives of the Proteaceae, although Chenery (1948, p. 180) lists 15 genera out of 20 tested in this family as aluminum accumulators.

Almost as remarkable is the Sweetleaf (*Symplocos*), a small tree; according to Chenery, one species of Sweetleaf, *Symplocos spicata* Roxb., contained 7.23 per cent Al (13.65 per cent Al_2O_3) dry weight in the leaves, the largest proportion found by him.

The work of Chenery established 1821 species of plants—out of a total of 4345 tested—as aluminum accumulators—*i.e.*, having more than 0.1 per cent Al (dry weight) in the leaves. Quantitative data are not given, however, except for the two highest values: 7.23 per cent Al in *Symplocos spicata* Roxb. and 6.61 per cent Al in *Miconia acinodendron* (L.) Tr. Chenery notes that aluminum is essential to the growth of aluminum accumulators and is available to the plant only in acid soils; he also observes that the cell-sap acidity range of these plants is quite narrow, pH 3.6 to pH 5.2.

It is evident that many kinds of vegetation, especially some of the tropical plants, may remove large amounts of aluminum from the soil. As the ratio of alumina to silica in unweathered rock is normally less than 1 to 3 and quite commonly less than 1 to 5 in siliceous rock, any plant in which the ratio of alumina to silica in ash is greater than 1 to 3 is probably depleting the soil of aluminum faster than it is of silica.

A few species of plants have an unusually high iron content. An analysis of the ash of the giant horsetail *Equisetum telmateia* (Ehrh.) showed 23.4 per cent Fe_2O_3, and an analysis of field horsetail *Equisetum arvense* (L.) gave 37.35 per cent Fe_2O_3, according to Mariani (1888); water chestnuts have almost as much iron (Table 1), and common garden lettuce may contain as much as 0.69 per cent Fe_2O_3 dry weight (Beeson, 1941, p. 142). Pobritskaya shows that the lichen *Parmelia* accumulates much iron (Jacks, 1953). Accumulators of iron are uncommon, however, and seem much less likely to be of geologic importance than do SiO_2 and Al_2O_3 accumulators. Chenery (1948, p. 174) noted only one iron accumulator—*Duroia longifolia* (P. and E.) Schm.—while testing more than 4000 species of plants for aluminum.

As is well known, the accumulators of calcium, potassium, and phosphorus are legion, but the possible geologic importance of their work has been neglected.

Geologic Potential of Silica-Accumulator Plants

It is of some interest to calculate the amount of silica that might be withdrawn from soil by suitable silica-accumulator plants under favorable conditions in the tropics. According to Bear (1955, p. 201–202), tropical forests produce from 10 to 20 tons dry weight of new growth per acre above ground each year, and forests in temperate climates produce about 2 tons. Approximately half of the new growth is in the leaves.

The amount of soil and rock affected by micro- and macroplants is largely determined by the depth of the root system of the higher plants, and the vertical distribution of organic nutrients chiefly controls the abundance of the micro-organisms of the soil biota. The roots of grasses and annuals are confined to a relatively shallow zone, but the roots of trees and other perennials may extend to depths of 20 to 100 feet; commonly the roots reach down to the level of permanent ground water in moist climates. Where the water table is shallow the root system spreads laterally, even though the plant has a tap root. Weaver (1954) describes burr oaks 50 to 65 years old, 12 to 18 inches in diameter, and 35 to 40 feet high, which had tap roots about 14 feet long but lateral roots extending 20 to 60 feet away from the tap root and to the same depth. According to Russian workers as summarized by the Soviet geochemist, Ginsburg (1957, p. 138), 75 per cent or more of the roots of spruce and pine near Moscow is concentrated in the upper 16 inches of the ground, and the bulk of the roots of most trees (in this area) is in the upper 2 feet. Few of the trees in this climatic zone reached depths in excess of 20 feet, but in general deciduous trees are able to assimilate material from deeper layers than are conifers.

In more arid regions much greater depths of penetration were observed. Meinzer (1927) and Robinson (1958) give much relevant information about the root system of the phreatophytes—plants that depend for their water supply on ground water. At least 70 plants that are common in the western United States are phreatophytes. The root systems of some of these

plants extend downward more than 100 feet, and depths of 50 to 75 feet are common. Raivitscher (1948) in a study of the water economy of the vegetation of the Campos Cerrados of southern Brazil notes that the trees have roots extending to the level of permanent ground water 18 meters below the surface.

It is difficult to obtain reliable information on the depth of tree roots in tropical areas, but Meinzer (1927, p. 5) notes that in rugged limestone regions of Cuba, where there was a heavy precipitation but little soil, he found tree roots that extended down along a vertical cliff about 100 feet into a perennial stream where it emerged from a cavern, but the long roots had functional roots only where they dipped into the stream. Mr. Gordon J. F. MacDonald of the U. S. Geological Survey (personal communication) informs me that he has observed the living roots of the Ohia tree in lava tubes 60 feet below the surface, a depth reached by growing down along joints and crevices in much jointed basaltic lava. All the ground—and rock—within reach of plant roots or micro-organisms is open to the attack of powerful biochemical leaching processes.

The annual leaf fall from trees is commonly about 1 to 1½ times the weight of the new growth of woody parts above ground; the leaf fall may take place continuously as in rain forests, chiefly during a fairly lengthy but definite dry season as in monsoon climates, or abruptly at the start of a cold season as with deciduous trees in cold temperate zones. This annual increment of vegetal matter is impressive, but to it must eventually be added the old growth itself, not only of the parts above ground but of the roots as well. The mineral content of the decaying roots, however, is far less vulnerable to erosion than is that of the superstructure. The ratio of roots to tops varies with age, species, and habitat; in general, the ratio is greatest for young plants in which it may exceed 1:1 and least in old trees in which it may be less than 1:5. Data from Evdokimova (1955) show for oaks a 1:1 ratio in 20-year trees, and about 1:4 in 45-year and 100-year trees—e.g., $\frac{6.39 \text{ kg}}{7.21 \text{ kg}}$, $\frac{43.97 \text{ kg}}{197.84 \text{ kg}}$, and $\frac{123.29 \text{ kg}}{457.31 \text{ kg}}$. In dry regions the ratio tends to be greater than in moist areas.

If we assume a growth of silica accumulators in the tropics that averages 2.5 per cent of silica (dry weight) and produces approximately 16 tons dry weight per acre per annum, it is evident that such a growth would abstract from the soil about 0.4 ton of silica per acre per year. This is equivalent to 1 ton of silica per acre each 2½ years, but, as noted earlier, it has already been established that silica is taken up at a faster rate than this by cane on sugar plantations in Hawaii.

To appreciate what such a rate may mean geologically, let us consider the amount of silica present in 1 acre foot of basalt having a density of about 3 and a silica content of 49 per cent (Table 2). This basalt, weighing 4080 tons per acre foot, would have 2000 tons of silica per acre foot. It is thus apparent that silica-accumulator vegetation—neglecting the weight of the roots—would use in 5000 years silica equivalent to the amount in 1 acre foot of basalt; possible but extreme figures of 20 tons dry weight per acre per year of vegetation containing 10 per cent silica would reduce the time to 1000 years, considering only the parts above ground. If 25 per cent is added for the roots, a probable extreme limit of 1 acre foot in 800 years is reached, but this does not consider the additional dissolved silica exported through the normal movement of ground water, which probably amounts to about 0.15 ton per acre per year. How much of the silica is exported and how much is recycled through generations of plants is unknown at present, but the data reviewed in this paper may help those who wish to speculate on the matter.

Chemical Exports from Weathering Rock

The chemical composition of soils derived by weathering of rock in place gives little clue as to the actual amount of various elements that have been removed during the process, and it is usually very difficult to arrive at a satisfactory estimate of the weight of fresh rock represented by a unit weight of residual soil. Commonly it is assumed that some element has remained static during weathering, but some estimates based on other assumptions have appeared in the literature and show a general agreement. Hawkes and Lakin (1949) estimate that three volumes of limestone have weathered to form one volume of residual clay near Friends Station, Tennessee, because of the change in dip of a certain horizon on passing from the limestone into residual clay. If the bulk density of the limestone is about 2.7 and that of the clay is 1.5, each unit weight of residual clay represents approximately 5 unit weights of the parent limestone.

The change of basalt to residual soil has been studied in the Hawaiian Islands by many

investigators, and Palmer (1931, p. 253–259) presents a strong argument for the belief that the alumina content of the completely weathered shells of some relict boulders has remained nearly constant throughout the process. The change in weight per unit volume is not considered, and the weight per cent alone suggests an almost three-fold increase in the alumina, and three unit weights of parent basalt would thus be required for one unit weight of residual soil. The work of Sherman and Uehera (1956) on the weathering of different mineral components of olivine basalt in Hawaii shows that the transformation of unweathered olivine to a plastic clay suggests a slight loss of Al_2O_3 relative to iron during weathering, but the iron content indicates a loss in weight per unit volume of 2.75 to 1. If TiO_2 is static during the weathering of the Kaui basalt (Table 2) the loss is about 4 to 1, but no density measurements were made.

TABLE 2.—COMPOSITION OF BASALT AND SOILS, KAUI, T. H.*

	Depth of soil in inches					
	S, 0–4.[1]	S, 4–16.[2]	S, 16–33.[3]	S, 33–180.[4]	S, 180–240.[5]	Basalt[6]
SiO_2	9.86	9.17	9.80	9.87	32.75	48.99
Al_2O_3	23.41	24.44	23.10	28.92	23.97	13.73
Fe_2O_3, FeO	34.86	35.84	39.83	35.36	20.96	1.60, 10.46[7]
MgO	0.36	0.32	0.26	0.17	2.44	13.53
CaO	0.34	0.27	0.21	0.17	3.77	7.34
Na_2O	0.02	0.00	0.01	0.00	0.34	1.62
K_2O	0.22	0.21	0.13	0.06	0.21	0.27
H_2O^-, H_2O^+	24.07[8]	22.59[8]	19.89[8]	19.66[8]	11.15[8]	0.10, 0.27
CO_2						0.24
TiO_2	6.55	6.89	6.42	5.54	3.54	1.73
MnO	0.15	0.15	0.10	0.22	0.24	0.20
SO_3	0.68	0.32	0.33	0.44	0.37	0.10
P_2O_5	0.36	0.37	0.37	0.40	0.45	0.13
Total[9]	100.58	100.22	100.21	100.45	99.62	100.38
Organic C	8.80	7.35	5.37	2.52	0.83	n.d.
N^-	0.27	0.17	0.08	0.03	0.02	n.d.

* Soil from pasture land covered with dense growth of *Paspalum* grass, central northern Kaui, T. H.; land may have been used for growing sugar cane 50 years earlier.

[1] Kaui soil, 0–4 inches, profile No. 2 (Hough and Byers, 1937) rainfall 80–100 inches, elevation about 500 feet; grayish-brown, red-flecked clay.

[2] Kaui soil, 4–16 inches, profile No. 2 (Hough and Byers, 1937); grayish-brown clay.

[3] Kaui soil, 16–33 inches, profile No. 2 (Hough and Byers, 1937); reddish clay.

[4] Kaui soil, 33–180 inches, profile No. 2 (Hough and Byers, 1937); yellowish-red loam plus clay, showing outlines of decomposed rocks.

[5] Kaui soil, 180–240 inches, profile No. 2 (Hough and Byers, 1937); well-decomposed but compact pieces of yellowish-brown lava.

[6] Calcic plagioclase-olivine basalt lava, tunnel 24, Olekele ditch, Kaui, T. H. (Cross, 1915).

[7] Total iron as Fe_2O_3 would be 13.22.

[8] Loss on ignition; includes organic matter.

[9] Total for basalt includes determinations for several minor elements not shown here.

The lateritic soil formed by the weathering of basaltic lavas in Hawaii may have a bulk density of less than 1—about one-third of that of the basalt (H. W. Lakin, oral communication), and virtually all the elements residual from the original basalt show a net decrease *per unit volume*. The changes shown in Table 2 should be considered with this problem in mind. A basalt containing 3×0.14 grams Al_2O_3 per cc changing into a soil containing

1×0.24 grams Al_2O_3 shows a net loss of $0.42 - 0.24 = 0.18$ grams per cc.

If we assume that a figure of 3:1 is a fair approximation for the weight ratio of parent rock to residual soil produced by strong weathering of igneous rocks, it is evident that the casual reader might be misled by a comparison of analyses of soil and bedrock, which are customarily given in weight per cent only. On the assumption that nearly all the inorganic constituents are the residual legatees of the amounts present in the rock, the figures for both soil and rock must be multiplied by their bulk density to get the content in grams per cc before an intelligent comparison is possible. Even though the analyses of a residual soil (bulk density 1) and its parent rock (bulk density 3) were identical in certain constituents, approximately twice as much material must have been removed as was left in the soil. Such losses—when recognized—are universally ascribed to leaching by vadose or ground water. The question I wish to raise is how much of this chemical loss is first *upward*—not downward!

Readily soluble inorganic constituents of soils and plant debris may be carried down to the water table, recycled, fixed in caliche, or, in some cold humid climates, moved quickly by surface runoff into near-by streams as constituents of relatively unleached litter. The less soluble constituents would linger at the surface but eventually would either be moved by erosive agents or become incorporated into the soil.

Although the lateritic soil developed on basalt represents only about one-third the weight of the fresh parent rock, volume for volume the laterite and the parent basalt may be nearly equivalent. In such lateritic soil, containing about 10 per cent SiO_2, there would be approximately 135 tons of silica per acre foot residual from the 2000 tons of SiO_2 in 1 acre foot of fresh basalt. The hypothetical tropical growth of silica-accumulator plants would require $2.5 \times (2000 - 135)$ years or about 4660 years to convert 1 acre foot of fresh basalt to 1 acre foot of this lateritic soil, if silica were removed solely through the agency of these plant accumulators. For the nearly uniform and complete weathering shown by the first 15 feet of the Kaui soil (Table 2), some 70,000 years would be required. Under optimum conditions, with a lush growth of high-silica accumulators such as a giantreed, bamboo, or representatives of *Moquilea*, such a soil might form in less than 15,000 years!

The conversion of granite gneiss to deeply weathered residual clay was studied by Goldich (1938) who notes that the zircon content of the residual clays increases with the intensity of weathering although the individual grains show some evidence of alteration. Unfortunately the bulk density of the samples is not given, and it is difficult properly to appraise the significance of the weight percentage figures given by Goldich (1938, p. 29). If the figures given in his Table 4 are converted to weight per cent, the zircon content shows a drop in the upper part of the C zone but increases substantially from 288 ppm in the fresh rock to a maximum of 946 ppm in the intensely weathered rock represented by sample 6. This suggests that something more than 3 unit weights of the parent gneiss is represented by 1 unit weight of the weathered residual clay, but Goldich notes that the parent rock may not be uniform in composition, and correlation of soil samples with fresh rock is thus somewhat uncertain.

Harrison's data on the seepage water and the weathering of the granite at the Mazaruni quarry in British Guiana are also worth attention, especially if interpreted in the light of possible biochemical movement of elements—a factor that was not considered at that time (Harrison, 1934, p. 66–79). A completely fresh section was sampled from the freshly blasted granite at the bed of the quarry to the soil about 18 feet above; the various zones recognized and their compositions are shown in Table 3. Harrison visited the quarry in 1919 during a period of exceedingly heavy rainfall and was able to collect water seeping from the face of the quarry at two places; the first, water A, was just above zone 3, the zone of active kaolinization, and the second, water B, was on a surface of the unaffected granite just below the zone of disintegration. Water A had percolated through 23 feet of argillaceous granite sand, and water B had percolated through 14 feet of argillaceous granite sand and then on through the zones 3 and 2 of active kaolinization and of disintegration of the granite. Water A accumulated at the rate of 1 liter in 2 hours, B at a rate of 1 liter in 3 hours. The chief differences between water A and water B are the much lower content of silica in B—9 ppm as contrasted with 19 ppm—and the appreciable increase in carbonate, calcium, and sodium. The nitrate, carbonate, and NH_4 in water B testify to the activity of nitrate-seeking roots of the higher plants. The seepage water from both zones contains an appreciable amount of

silicon and iron but only a trace or less of aluminum. For this reason, aluminum may be regarded as a static constituent for the purpose of getting a minimum figure on losses per unit volume, unless other considerations indicate that a different constituent is a better index of the chemical losses. Harrison's posthumous paper contains no figures on bulk densities, but Table 3 indicates that more than half the original rock has disappeared during its weathering to clay subsoil.

In the zone of decomposition just above the granite, the rock is soft, brownish, and somewhat incoherent, but nevertheless clearly recognizable as granite; in this zone the feldspar oligoclase ($CaAl_2Si_2O_8$, $4NaAlSi_3O_8$) is almost completely broken down, and the other components were somewhat attacked. As both seepage waters are very much undersaturated with respect to silica, there is little probability that silica was precipitated as quartz in the zone of decomposition, and it is far more likely that some aluminum was lost than that quartz was added; for this reason I have taken the apparent increase in quartz between the zone of decomposition and the unaltered granite as an index of the minimum losses in calculating the figures shown in Table 4, and it is assumed that quartz is static between zones 1 and 2. In the higher zones the greatest change in weight percentages is in alumina, and, on the assumption that this

TABLE 3.—COMPOSITION IN WEIGHT PER CENT OF RAIN WATER, SEEPAGE WATER, AND ZONES OF ALTERING GRANITE, MAZARUNI QUARRY, BRITISH GUIANA

	1 ppm	2 ppm	3 ppm		4	5	6	7	8	9
SiO_3	0.09	24.00	11.60	SiO_2 (insoluble)	31.66	41.20	41.67	37.27	31.45	39.90
TiO_2	....	tr.	tr.	SiO_2 (soluble)	41.07	32.71	28.50	29.76	30.98	29.80
Al	0.03	tr.	....	Total SiO_2	72.73	73.91	70.17	67.03	62.43	69.70
Fe	0.15	2.52	1.40							
Mg	0.31	0.98	0.73	Al_2O_3	14.45	15.05	18.84	21.19	24.44	23.20
Ca	0.76	3.60	5.00	Fe_2O_3	1.41	1.77	1.78	1.72	1.55	1.58
Na	1.51	3.31	5.72	FeO	0.50	0.49	0.25	0.29	0.27	0.05
K	0.18	3.62	3.45	MgO	0.82	0.44	0.17	0.32	0.22	0.17
CO_3	0.95	13.00	16.42	CaO	1.03	0.22	0.03	0.11	0.02	0.01
SO_4	1.27	....	tr.	Na_2O	2.83	1.90	0.21	0.14	0.12	0.10
Cl	2.93	5.70	3.90	K_2O	4.82	3.86	2.70	2.20	1.35	0.47
NO_3	0.86	2.70	2.60	H_2O	0.68	1.71	5.17	6.35	8.64	4.71
NH_4	0.02	0.09	0.08	TiO_2	0.67	0.66	0.68	0.65	0.84	0.94
				P_2O_5	0.06	....	.....	.....	....	....
				MnO	0.23	tr.	.....	.....	....	0.01
Total salinity	9.093	59.52	50.90	Total	100.23	99.99	100.00	100.00	99.88	100.94

1. Average of analyses of 3 years' rainfall, Georgetown, British Guiana, (Harrison, 1934, p. 15).
2. Sample of percolating water A seeping from zone of completed kaolinization (Harrison, 1934, p. 79).
3. Sample of percolating water B traversing all the zones of alteration and collected on the surface of granite from quarry face (Harrison, 1934).
4. Zone of unaffected granite exposed to depths of 3 feet 2 inches (Harrison, 1934).
5. Zone of softening and disintegrating granite, average of 4 analyses of successive portions of the zone, total section 1 foot 11 inches (Harrison, 1934).
6. Zone of active hydration and kaolinization, 6 inches thick, lying above 5 (Harrison, 1934).
7. Zone of "gradually continuing hydration and kaolinization", 9 feet 8 inches thick, average of 10 analyses of successive portions of zone (Harrison, 1934).
8. "Zone of more or less completed kaolinization", 1 foot 10 inches thick, average of 2 analyses (Harrison, 1934).
9. Topsoil, 8 inches thick (Harrison, 1934).

TABLE 4.—ALTERATION OF MAZARUNI GRANITE CALCULATED IN QUANTITIES PER 100 GM VOLUME OF FRESH ROCK*

	1	2	3	4	5	6
SiO_2 in quartz	31.66	31.66	25.66	20.40	14.93	19.95
Soluble SiO_2	41.07	25.43	17.55	16.29	14.70	14.90
Total SiO_2	72.73	56.79	43.21	36.69	29.63	34.85
Al_2O_3	14.45	11.60	11.60	11.60	11.60	11.60
Fe_2O_3	1.41	1.36	1.10	.94	.74	.79
FeO	.50	.38	.15	.16	.13	.02
Fe as Fe_2O_3	1.96	1.78	1.27	1.12	.98	.82
MgO	.82	.34	.10	.18	.10	.08
CaO	1.03	.15	.02	.06	.01	.005
Na_2O	2.83	1.46	.13	.08	.06	.05
K_2O	4.82	2.97	1.66	1.20	.64	.23
H_2O	.68	1.31	3.18	3.48	4.10	2.35
TiO_2	.67	.51	.42	.36	.40	.47
MnO	.23	trace	...	...	...	.005
	100.17	76.87	61.57	54.75	47.41	50.00

1. Fresh granite.

2. Zone of soft decomposing brownish granite, 1 foot 11 inches thick.

3. Zone of active kaolinization, thin gray shaly layers of crumbly granite, 6 inches thick.

4. Zone of kaolinizing granite sand, 9 feet 6 inches thick.

5. Zone of kaolinized argillaceous granite sand, 1 foot 10 inches thick.

6. Topsoil, loose sandy pebbly soil, 8 inches thick.

* Calculated by T. S. Lovering from data given by Harrison (Table 3).

oxide remains static from zone 2 to the surface, minimum losses can be computed per unit volume.

Certain features in Table 4 are of considerable interest. Silica decreases steadily from the fresh rock up to the soil, but the 8-inch soil layer shows a significant increase. Iron, on the other hand, decreases consistently from the fresh rock to and including the soil. The detailed analyses of parts of zones 4 and 5 given by Harrison show that calcium increases appreciably in a zone extending from about 5 feet to about 10 feet below the surface, where it averages nearly 0.10 per cent by volume or 0.16 weight per cent. The substantial increase in the content of silica in the soil at the surface—where the relatively insoluble silica phytoliths would accumulate—the decrease in the amount of silica in water B at the bedrock surface just below the zone of decomposition, and the content of nitrate in water B all are in harmony with the suggestion that silica is being abstracted by plants through their roots, carried up by them to the surface vegetation, there to become available in part for recycling in the upper part of the percolating ground water and in part to become subject to removal through runoff. The very perceptible increase in calcium at a depth of 5 to 10 feet probably represents migratory calcium derived from decomposition of plant liter.

Harrison's work on the laterization of the basic and intermediate rocks tells the same general story as does the study of the kaolinization of the granite. The transition from unaltered basic rock to primary laterite is much more abrupt than the transition from unaltered granite to the kaolinized granite sand, and there is substantial evidence of the movement of both silica and alumina in the laterites. Silica, of course, decreases sharply in the primary laterite, then increases in the overlying lateritic earths, and reaches a maximum at the gray sandy subsoil and soil at the surface. Calcium also, which drops from nearly 10 per cent to nil in the primary laterites and the lateritic earth, is perceptible in the subsoil. The removal of material at depth and its reappearance at the surface strongly suggest the activity of plants. The difference between a siliceous bauxitic laterite and a low-silica bauxitic laterite may be due in some places to the difference in effectiveness of the runoff in removing the plant litter that carries the silica brought to the surface by vegetation.

SILICA IN TROPICAL GROUND WATER

Krauskopf (1956, p. 15, 24), after a thorough study of the literature supplemented by experimental work, concludes that in the great majority of natural waters silica is present in true solution only, and he shows that the solubility of silica in true solution at a temperature of 25° C. (77° F.) is 135 ppm. He attributes the undersaturation of silica in terrestrial waters to the slowness with which silica and silicates dissolve and to the activity of organisms that use silica. In some experiments which I per-

formed many years ago (Lovering, 1923) the solubility of several silicates—greenalite, actinolite, glauconite, and various forms of silica such as chalcedony, opal, and quartz—was tested at room temperature in a number of solutions. Equilibrium was not attained in several months, and except in markedly alkaline or acid solutions the solubility of the silicates and opal commonly ranged between 20 and 80 parts per million. Excluding the strong inorganic acids and alkalies, "humic acid" (an unsterilized aqueous extract of peat) showed the strongest solvent action and dissolved 80 ppm of silica from glauconite in a little less than a year.

Clarke (1924, p. 95 *et seq.*) gives the silica content of many waters from rivers draining tropical forests, and in general the silica content ranges between 10 and 40 ppm—nearly twice as much as in rivers of temperate North America. For high rainfall the figures tend to drop, and for low rainfall to increase. However, in British Guiana, where the rainfall is high (100 to 150 inches per year) rivers draining areas undergoing laterization carry about 25 ppm SiO_2 (Harrison, 1934).

The biennial reports of the Board of Water Supply, Honolulu (1953; 1951), give interesting and suggestive data on the composition of vadose and ground water used for the city of Honolulu, where the rainfall is more than 100 inches per year. Some of the water is obtained from shallow tunnels known as "skimming tunnels," which are driven about at the top of permanent ground water; the water thus utilized has had little time to remain in the semistagnant zone of ground water—these tunnels take instead vadose and ground water where circulation is most active. The water from the skimming tunnels averages about 12 ppm SiO_2 and ranges from 8 to 16 ppm. Some water comes from large springs, which, as with the supplies from the tunnel, represent very active ground-water circulation but presumably utilize water that has been in contact with the rocks for a somewhat longer period of time than that in the tunnels; this water averages about 20 ppm SiO_2. A substantial part of the water utilized, however, comes from shafts sunk well below the ground-water table and has been in contact with the rocks for a much longer period of time than water from the tunnels or the springs; the silica content of this water averages about 38 ppm (range 36 to 41 ppm). An analysis of water taken from the Waiahole tunnel, which taps deep ground water impounded back of a dike under the Kaolau Range, showed 74 ppm SiO_2. The shafts and the tunnels are driven in the basaltic bedrock of the island, and the samples are representative of the ground water in this area. The concentration of silica seems unrelated to salinity but related rather to the probable length of time that the water is in contact with bedrock.

Harrison (1934) found 12.5 ppm SiO_2 in spring water from the surface of a laterizing epidiorite in British Guiana, and 33 ppm of SiO_2 in water seeping into a tunnel 180 feet below the level of the laterizing surface of its metamorphic equivalent, a hornblende schist (Table 5). These figures are strikingly similar to those in water in comparable situations in the basaltic rocks of Hawaii, the composition of which is given in Table 2.

The data given above suggest that the silica content of vadose water near the surface, in tropical areas having moderately heavy rainfall, approximates 10 to 15 ppm but increases with time of contact and distance traveled under the ground and commonly is 20 to 40 ppm in the ground water. The amounts found reflect the slowness with which equilibrium conditions are attained in the solution of silica from rock or soil when biochemical activity is minimal.

Transpiration and Circulation of Water by Silica-Accumulator Plants

The amount of silica dissolved in ground water should be considered in seeking an understanding of the source of the silica taken up by vegetation. Most of the water—more than 95 per cent—taken up by vegetation normally is lost by transpiration. In the work of Mohr and Van Barren on tropical soils (1954, p. 54 *et seq.*) evidence is presented that the transpiration of tropical forests probably approximates between 1000 and 3000 mm (39.4 and 118.1 inches) of water per year, but that a luxuriant forest with excess rainfall and moderately high temperatures may transpire from 3000 to nearly 5000 mm of water per year. If we assume that about 2000 mm (78.7 inches) is a safe average (bamboo forests are quoted as 1500 mm on the average, 3000 mm for luxuriant growth), we conclude that a tropical forest, such as the hypothetical forest of silica accumulators assumed earlier in this paper, may transpire about 80 inches of water annually.

Let us assume that 15 ppm of silica is available in true solution in vadose water to the

silica-accumulator plants in the tropics, and further assume that the equivalent of 80 inches of rain from a total rainfall of 150 inches moves up through the forest vegetation and is lost through transpiration; it then follows that about 9000 tons of water would be transpired per acre by this hypothetical forest, but something less than 5 per cent of this might be recirculated from leaves to roots (Crafts *et al.*, 1949, p. 174, 176). This recirculated water would add nothing from ground water, however, and so approximately 0.000,015 × 9000 tons or 0.135 ton of silica would be available in true solution to the vegetation from the vadose water taken in through its roots. These figures show that the amount of silica calculated as removed from tropical soils by silica accumulators—e.g., 0.4 to 1.5 tons per acre per year—would require that biochemical factors accelerate the solution of SiO_2 well above the figures normal for vadose water even where there is ample evidence that laterization is active. If we assume that about 45 inches of precipitation finds its way to the water table and thence to the streams and carries about 30 ppm SiO_2, some 0.15 ton of SiO_2 per acre would be moved by ground water. If to the 0.4 ton ascribed to vegetation is added the 0.15 ton of SiO_2 per acre per year carried by ground water, a reasonable rate of

TABLE 5.—COMPOSITION OF WATER FROM LATERIZING BASIC ROCK, BRITISH GUIANA, AND COMPOSITION IN WEIGHT PER CENT OF LATERIZING HORNBLENDE SCHIST

	ppm			Weight per cent			
	1	2		3	4	5	6
SiO_3	15.84	41.80	SiO_2 (insoluble)	4.30	4.99	11.14	19.05
Al	1.06	0.28	SiO_2 (soluble)	45.45	7.38	8.27	21.71
Cl	6.03	6.48					
Fe	0.28	2.54	Total SiO_2	49.75	12.37	19.31	30.76
Mg	3.11	18.25					
Ca	2.47	38.03	Al_2O_3	12.18	34.77	30.81	23.28
Na	3.45	4.92	Fe_2O_3	0.03	22.04	24.41	18.33
K	0.11	0.71	FeO	9.88	2.85	1.46	1.34
HCO_3	9.00	75.97					
SO_4	.....	0.33	Fe as Fe_2O_3	11.00	25.22	26.03	19.82
NO_3	.39	7.66					
NH_4	.....	.....	MgO	9.54	1.57	0.07	0.03
			CaO	11.79	0.06	0.01	0.01
			Na_2O	1.19	0.33	0.12	0.03
			K_2O	1.19	0.23	0.08	0.09
			H_2O	0.35	20.76	19.38	13.75
			TiO_2	4.60	4.93	4.21	2.59
			MnO	0.48	0.01	0.06	0.06
			P_2O_5	0.06	0.08	tr.	tr.
Total salinity	41.75	196.82	Total	99.96	100.01	99.96	100.28

1. Spring water from Issorora; water that has passed over the surface of an epidiorite undergoing laterization (Harrison, 1934, p. 13).

2. Seepage water in tunnels at Peter's Mine, water that has percolated through laterizing hornblende schist tunnel about 180 feet below the level of the altering rock surface (Harrison, 1934, p. 13).

3. Fresh hornblende schist, 35 miles south of Punda Palya, British Guiana, probably a metamorphosed diabase (Harrison, 1934, p. 31).

4. Transitional layer of adherent primary laterite, 0.2 inch (Harrison, 1934, p. 31).

5. Primary laterite above No. 4, 3 inches thick (Harrison, 1934, p. 31).

6. Gravelly lateritic earth above No. 5, about 19 feet thick; No. 6 lies under 1 inch of surficial soil on which are scattered rocks of surficial bauxite and iron stone about 2 inches thick (Harrison, 1934, p. 31).

removal of silica—both upward and downward —would seem to be about 1 ton per acre in 2 years or less, but from this silica "loss" should be subtracted the unknown figure for the silica recycled in the plants.

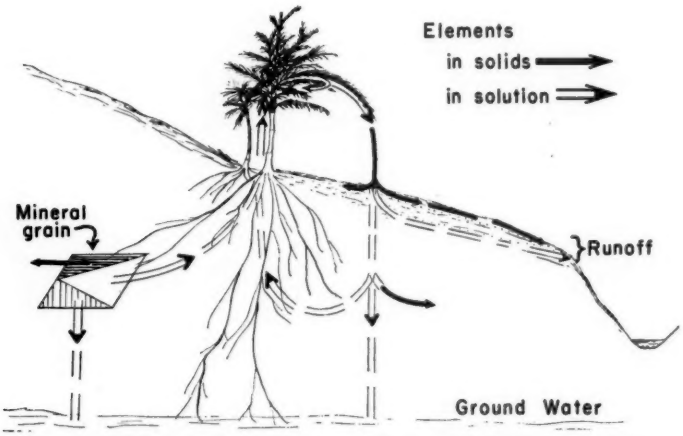

FIGURE 1.—ROUTES OF MIGRATION OF ELEMENTS IN DECOMPOSING ROCK

SURFICIAL EXPORT OF ORGANIC SILICA

It is, of course, unlikely that all the silica moving into plant accumulators is lost to the ground, and as shown in Figure 1 there are many routes that it may follow from a mineral grain to the river. There is much evidence that all silica secreted by living organisms is initially opaline (Smithson, 1956; Netolitzky, 1929) although it may be transported either as organic or inorganic compounds within the plant or animal. Nevertheless, whether the silica is present in the plant as opal, as fine-grained quartz, or as organic compounds, it may be highly vulnerable to chemical and physical erosion while the plant matter is decomposing. In regions of heavy precipitation a large percentage of the plant silica may be removed by surface water if high runoff occurs, whereas much of it would enter ground water in highly permeable soils.

The moisture regimen in areas of laterization is diverse, but these areas are alike in having warm climates and abundant rainfall. In rain forests where daily rains are the rule, much of the rain never reaches the ground; most of the moisture that gets through the heavy canopy of foliage is in the form of drip or drizzle with little erosive power and provides a minimum of runoff. According to Kerner-Marilaun (1927, p. 414), however, the optimum conditions for laterization obtain if a wet season marked by heavy precipitation alternates with a dry season, when the climate is uniformly warm the year around, and such conditions are common in tropical monsoon climates. In such climates runoff may be impressive.

Rhynsburger (1956, p. 43–54) reports some relevant observations on the rainfall and runoff in Taiwan. He notes that the average annual precipitation of 100 inches is statistically more than ample to keep all reservoirs filled, but that, unfortunately, it is not favorably distributed in time or space. The abundant summer rainfall "is so concentrated in short heavy downpours that a prodigiously large proportion runs off rapidly over the surface rather than replenishing ground-water reservoirs." A record rainfall of 4 inches in 1 hour was recorded at Hengchun in 1943, and rainfalls of 30 inches in 1 day are of almost common occurrence. Rhynsburger observes that "Regardless of the character of soil or vegetation cover, only a small fraction of these volumes of water can percolate downward or be absorbed, so that such intensive rainfall must be disposed of chiefly by surface runoff." A large movement of organic debris into the nearest stream would be inevitable. The brown and black waters of tropical rivers may in part reflect such concentrated downpours, but the silica content of the solid organic material in suspension is not known, as it is excluded by settling or filtering the water before analysis. Much of

the dark color, however, is caused by filterable organic material, the exact composition of which is unknown.

The silica secretions in grasses are released, apparently unaltered, as minute opaline hooks, rods, and equidimensional particles when the plant withers and decomposes, or when it is ingested and excreted by grazing animals or lower forms of life. Russian pedologists were probably the first to recognize opaline phytoliths—minute stony parts of a plant—in soils (Ruprecht, 1866; Usov, 1943; Tyurin, 1937), but recently Smithson (1958) has shown that grasses contribute vast numbers of opal phytoliths to British soil, commonly in particles 5 to 10 microns in diameter or in rods 2 to 10 microns wide and 5 to 50 microns long. Opaline phytoliths were found to be abundant in the dung of grazing animals. Low-density mineral particles of such shapes and sizes could be readily transported by either wind or water. In grasslands where fires are common during seasonal dry periods, wind-borne ash may leave the permeable terrane and in any event would be more easily and quickly moved by minor runoff.

Although silica accumulators have been emphasized above, it is quite apparent that accumulators of other elements could deplete the subsoil in them—rather than silica—if the ratio of the accumulated element to silica were greater in the plant than in the soil. The "export route" followed by the various inorganic constituents of the soil biota would depend entirely on the local total environment and on the chemical characteristics of the constituents.

Rennie has recently discussed the nutrient demand of various forest growths and presents figures for typical temperate zone stands that are suggestive (Rennie, 1955, p. 64) and are summarized in Table 6.

The figures given are conservative but show that the forests use from 40 to more than 100 pounds of Ca (56 to 140 pounds CaO) per acre per year. Much of this is normally recycled, but a substantial amount could be removed by runoff or ground water, or fixed in the vadose zone as a caliche.

Biochemical Factors

Botanists are well aware that plants may differ greatly in their selection of inorganic constituents, and that in part this can be ascribed to the character of the soil or rock on which the plant grows. Broadly speaking, however, the composition of the plant ash is primarily a characteristic of particular species, genera, or families. Most plants are well above average in some constituent and therefore can be regarded as accumulators of such constituents. Perhaps it would be well to discriminate between selective accumulators and merely tolerant accumulators, and also accumulators that are depletory with respect to a constituent of the soil. The hickory is a selective—and depletory—accumulator of rare earths in almost any soil, the catbriar is a tolerant accumulator of MgO—its ash contains 4 per cent in coastal plains woods and 17 per cent in serpentine barrens (Wherry, 1932)—but it is not necessarily depletory; giantreeds (70 per cent SiO_2 in ash), where growing on sandstone, are not depletory, but where they grow on average clay soil (30–50 per cent SiO_2) they are both selective and depletory. On the other hand, plants with only average requirements for elements such as phosphorus or potassium would also be depletory when growing on a serpentine barren.

Table 6.—Yearly Demand for Nutrients, Exclusive of Litter
In kg/acre

	Ca_w*	Ca_f*	K_w	K_f	F_w	P_f
Pines	2.03	16.	.91	16.0	.21	4
Other conifers	4.38	41.0	2.34	26.	.41	8
Hardwoods	8.79	26.	2.25	13.	.44	3
4 crops, agriculture†	9.80		30.00		4.30	

* Subscript w refers to woody parts, subscript f refers to foliage.

† Rotation of oats, grass, potatoes, and turnips is assumed, with yields of 0.8 ton, 1.5 tons, 6 tons, and 17 tons per acre respectively.

Some of the organisms most potent in breaking down rocks are apparently the lower forms of plant and animal life. Vinogradov and Boichenko (1942) investigated the process by which the diatoms *Nitzschia palea* and *Navicula minuscula* decompose nacrite—a clay mineral identical in composition with kaolinite but commonly occurring in coarser crystals. The nacrite proved to be an adequate source of silica for the diatoms in pure culture—with or without symbiotic bacteria—, and the decomposition of the crystals was observed under a microscope. The crystals started decomposing where they came in contact with the slime sheath secreted by the diatoms. The decomposi-

tion was accompanied by an increase in opacity, and the crystal swelled, lost its birefringence, and began to exfoliate along cleavage planes. Eventually the crystal became amorphous, irregular in outline, and diminished in size, while alumina was liberated into the medium, and silica was assimilated by the diatoms. As the decomposition of the nacrite was external to the diatom cell, it seems probable that some soluble silica would diffuse into the medium, although apparently nearly all of it was absorbed into the diatom itself.

Jacks (1953) summarizes the work of several Russian investigators on the earliest stages of soil formation from crystalline rocks; the studies are chiefly on the effect of pioneer organisms such as lichens and mosses on the decomposition of intermediate and acid igneous rocks. Unweathered rock at high altitudes was selected to avoid material already weathered by inorganic agents. B. B. Polynov and also Pobritskaya and Yarilova showed that the first stage of soil formation results from the attack of lithophyl lichens which produce an appreciable horizon of organo-mineral dust on the rock surface in a short time. The inorganic part of the dust is richer than the parent rock in phosphorus, magnesium, calcium, potassium, sulfur, and iron. The lichen *Gyrophora* collected much potassium, and *Parmelia* much iron. Glazovskaya showed that green and blue-green algae together with diatoms are very active weathering agents of the rocks of the high mountains and yield products of weathering that include both amorphous silica and calcite. Bolyshev studied the influence of algae on the formation of the alkaline takyr soils of arid regions and was able to show that blue-green algae—the only vegetation in the region!—when cultured on different soils were very effective in decomposing the soil minerals and bringing into solution both silica and alumina and, to a lesser degree, iron. The effect of *Amorphonostoc paludosum* (Kutz) Elenk was especially strong.

The chemical effect of the soil biota on its inorganic as well as its organic environment is tremendous, both qualitatively and quantitatively. Some appreciation of the chemical output of these unseen manufacturers of potent chemicals comes from figures on their bulk weight. According to Millar and Turk (1952), the top 7-inch layer of good soils in the temperate zone has a live weight of soil biota per acre as follows (in pounds):

Bacteria	700
Fungi	1000–1500
Actinomyces	700
Algae	? (100,000/gm)
Protozoa	200–300
Earthworms	200–1000
Total	2800–4200

or about 500 pounds per inch of depth.

The chemistry of the biologic reactions of these organisms with respect to SiO_2 is almost unknown but is most assuredly worthy of study. Thiel (1927) has shown the effectiveness of bacteria in causing the solution of aluminum from clay, and the work of Norkina and Pumpyanskay (1956) shows that certain silicate bacteria, in addition to their ability to release potassium from silicates, are capable of fixing some nitrogen. The effect of the soil biota on the composition of soil solution is presumably major near the surface, and it is apparent that the availability of the various chemical elements in the soil solution is an important factor in their movement into a plant, but much remains to be learned of the mechanisms of transfer of inorganic elements from soil to plant. The inorganic constituents are present in part as ions and in part as organic complexes in the soil solution.

There is a legion of organic complexes with which the analytical chemist is familiar. Some of these such as iron citrate, the ferric salt of citric acid, are extremely stable and tend to make iron nonreactive and thus remove it as an interfering element in solutions that contain other elements sought. Citric acid is a common decomposition product in nature and so are hundreds of other possible complexing organic compounds. The presence of many of these has long been established, and the presence of many others is assumed—quite properly.

Silica, alumina, and iron are absorbed by many kinds of higher plants, but the way in which these constituents move into the plant and through it is a matter of speculation. It has been observed, however, that iron chlorosis which commonly takes place in a soil having a high lime content is best combatted by adding an iron chelate to the soil.

It seems reasonable to assume that some of the usually insoluble constituents are moved into and through the plant in the form of organic complexes. As noted earlier, difficultly soluble mineral silicates such as feldspars, amphiboles, pyroxenes, and kaolinite or nacrite are rendered soluble by organic compounds generated in living lichens, algae, and diatoms, and the silica is absorbed by the organism.

It is known that organic silica complexes can be formed biologically; Louise Holzapfel showed the presence of tetracholesteroxysilane and its homologs in silicotic lungs. Together with Kerner-Esser, Holzapfel[1] found other silicon compounds in steers' blood.

It is now generally believed that the known acid reaction of root hairs—a result of cellular respiration—is instrumental in making H^+ ions available for exchange with the similarly charged cations in the soil—without the necessity of the base being in solution in ground water. Such action does not immediately explain the absorption of silica by plants, as virtually all ionized silicon compounds contain the silicon as a negatively charged ion, although it is possible—but not established—that some ionized silicon complexes may contain silicon in a positively charged complex ion. However, the glib explanation that silicon moves into plants as a soluble sodium silicate ignores the arresting effect of the acid reaction of the root hairs. The work of DeKock (1956, p. 136) shows that different metals may pass into roots in toxic amounts if the metals are present as ions in the nutrient solution, but that the plant may exclude them or take up only the optimum quantity if the metals are complexed. It therefore is of some interest to consider some of the biochemical factors that apparently influence the amount of silicon made available to silica accumulators, and the depths to which biochemical action would be effective.

The availability of certain inorganic constituents is of course profoundly influenced by the pH of the soil, and this in turn is responsive to the chemical characteristics of the litter or humus on the ground. It is well known that the decomposition of plant litter under sequoia, some pines, and oaks tends to reduce the acidity of the soil, whereas the humus under the beech and fir has the reverse effect (Table 7).

Rennie (1955, p. 82) found extremely acid litter under pine, birch, and ling growing in the same soil, but the litter showed very different amounts of soluble ("available") nutrients: *Pinus sylvestris*, pH 2.9, total Ca 0.50%, per cent of total Ca available, 20%; *Betula* sp., pH 3.2, total Ca 3.3%, per cent of total Ca available, 50%; *Calluna*, pH 3.1, total Ca 0.5%, per cent of total Ca available, 41%; the per cent of P that was determined as "available" was nearly the same for the different trees and for the shrub *Calluna*—*e.g.*, about 28 per cent.

It is generally believed that the rate of accumulation and of humification of organic resi-

TABLE 7.—VALUES FOR pH IN SOILS SUPPORTING VARIOUS TYPES OF VEGETATION

	No. of determinations	Range	Optimum for growth
Silver fir, *Abies pectinata*	11	3.5–4.7	3.98
Beech, *Fagus sylvatica*	17	3.6–6.9	4.88
Pyrenees oak, *Quercus toza* (O.)	3	6.1–6.7	6.46
English oak, *Quercus pedunculata*	14	5.4–7.8	6.50
Sequoia, *Sequoia gigantea*	1		7.20
Allepo pine, *Pinus halepensis*	38	6.8–8.5	7.66

Arranged according to increasing pH (Laiseca, 1949, pt. 1, p. 31)

dues in the A_0 layer is primarily dependent upon the climate, but to a very large extent it is also dependent upon the type of vegetation. Many types of woody plants are rich in resins and other organic substances that discourage bacterial and fungus activity. Although decomposition is chiefly the result of the activity of the micro-organisms, many macro-organisms such as insects and earthworms are also responsible for destruction of much A_0 material. The end product of these various organic processes, however, is the liberation of the mineral matter of the plant material either as insoluble pellets such as phytoliths or as soluble compounds available to percolating water. Biochemical reactions in grasslands differ materially from those in forests, but large variations should be expected for such widely differing ecological groups. Commonly the litter in forests shows a very material increase in silica over that found in the living foliage, but in the silver fir and the beech this is not true (Table 8).

The shallow-rooted ground flora under trees is responsive to the composition of the litter, and the amount of silica taken up reflects this factor in a striking way (Table 9).

Different silica accumulators may release silica in very different forms upon decay, and

[1] Referred to by H. W. Post (1949, p. 138). (The original article by Holzapfel was not seen by the writer.)

two experiments carried on recently by the U. S. Geological Survey are of some interest in this connection. Twenty-gram samples (dry weight) of pulverized *Ephedra* from Monument Valley, Utah, and a 20-gram composite of four samples of *Equisetum* from Alaska were allowed to decompose under water in polyethylene beakers held at a temperature of 30° C. and at 100 per cent humidity. Both the *Ephedra* and the *Equisetum* sample contained nearly 3 per cent silica dry weight—*e.g.*, the *Ephedra* contained 2.56 per cent SiO_2 dry weight, and the *Equisetum* 3.36 per cent. After 6 weeks of decomposition during which time the beakers were stirred daily, care being taken to contaminate each beaker with a drop or two of material from the other during each agitation, the material in each beaker was centrifuged, and the liquid filtered through number 42 Whatman paper. The extract from the *Ephedra* contained about 10 ppm SiO_2, whereas the extract from the *Equisetum* contained about 320 ppm silica—more than twice the amount in a saturated solution of amorphous silica in water!

Such differences in the solubility of silica in decomposing plant litter should profoundly affect the subsequent movement of the material, physically or chemically.

The entire history of silica—and other elements taken up by accumulator plants—is one of great interest, but any answers suggested at this time are speculative. Bacterial action in the litter is very rapid in tropical forests, and the CO_2 generated would be an effective agent for taking cations present into solution. Such basic cations as sodium and potassium in turn may help to increase the mobility of the silica, but the high solubility of the *Equisetum* silica in the experiments

TABLE 8.—CHANGES IN COMPOSITION OF ASH OF PLANTS WITH AGE AND DECOMPOSITION

(In weight per cent)

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
SiO_2	1.2	13.4	20.7	24.4	28.65	34.55	31.01	4.41	33.34	30.95	20.17	45.01	16.79	57.02
Fe_2O_3	n.d.	n.d.	n.d.	n.d.	.88	1.33	3.14	1.18	2.31	0.61	1.63	2.97	2.60	2.80
MgO	n.d.	n.d.	n.d.	n.d.	.7.45	4.06	6.56	13.53	9.23	3.96	8.30	4.45	10.43	6.91
CaO	9.8	26.5	34.0	34.1	29.12	40.65	45.31	26.09	37.15	48.63	20.47	39.81	26.44	21.98
Na_2O	n.d.	n.d.	n.d.	n.d.	1.63	0.20	1.06	n.d.	2.78	0.61	1.38	1.03	1.52	1.36
K_2O	30.0	10.7	4.9	1.0	20.17	7.69	4.90	33.14	7.47	3.35	29.61	3.32	22.75	4.57
P_2O_5	24.2	5.2	3.5	1.9	8.38	5.70	5.16	12.19	4.30	8.08	14.73	4.99	16.24	3.74
Mn_3O_4	n.d.	n.d.	n.d.	n.d.	.98	.23	.74	6.60	1.92	n.d.	1.02	0.43	n.d.	n.d.
Ash	n.d.	n.d.	n.d.	n.d.	4.91	7.05	5.43	3.50	5.36	4.90	2.55	4.61	3.53	3.99

1. Beech leaves, May 16
2. Beech leaves, July 18
3. Beech leaves, October 14
4. Beech leaves, November 30

(Laiseca, 1949, pt. 1, p. 18)

5. Beech leaves, August (13 analyses)
6. Beech leaves, November (7 analyses)
7. Beech leaves—litter (23 analyses)

(Wolff, 1880, p.129)

8. Oak leaves in August
9. Oak leaves, decayed
10. Oak leaf litter

(Wolff, 1880, p. 130)

11. Spruce needles on tree
12. Spruce needles, litter
13. Larch needles on tree
14. Larch needles, litter

(Wolff, 1880, p. 131)

TABLE 9.—PERCENTAGES OF SiO_2 CONTAINED IN THE GROUND FLORAS (OVEN DRY) UNDER DIFFERENT TREES

Trees	SiO_2 (insoluble residue) in composite sample of flora under tree
Alder *Alnus incana*	14.95
White birch *Betula alba*	15.66
Larch *Larix leptolepsis*	7.83
Beech *Fagus sylvatica*	6.22
Oak *Quercus robur*	5.54
Douglas fir *Pseudotsuga taxifolia*	5.20
Larch *Larix decidua*	1.86
Pine *Pinus sylvestris*	1.36

Arranged according to SiO_2 content (Ovington, 1954)

cited was observed in a solution having a pH less than 7—a pH that excludes the possibility of a soluble basic silicate. The micro-organisms responsible for the biochemical activity were presumably microbial rather than algal, and such activity could persist deep in porous ground. It seems quite probable that some of the leaching in the lower part of deep laterites should be ascribed to inorganic leaching, but the activity of organisms in such water has been established, and the movement of silica into solution may be greatly accelerated through the biochemistry of micro-organisms. At shallow depths, the role of organisms in causing the solution of silica is believed to be dominant wherever the vegetation is lush. If conditions favor the preservation and accumulation of insoluble phytoliths of siliceous vegetation, as on prairies, the A horizon may become enriched in SiO_2 from plants that pump it out of the B horizon. Under other conditions, silica made soluble during decomposition of litter in tropical jungles would be available to vadose water for removal through ground water, for recycling through plants, or for resilication of the upper part of the profile of laterization; this latter silica may be liberated in part by organic agents and in part by changes in soil moisture that reflect the alternation of the wet and dry seasons. Although there must always be a certain proportion of the SiO_2 that is recycled or added to groundwater circulation, nevertheless, under favorable conditions, substantial quantities of silica must be pumped out of the ground at depth, spread over the surface in the organic debris, and then swept off by erosive agents.

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